Transport and fate of veterinary sulfonamide antibiotics in soil

Dissertation

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Abstract

Sulfonamide antibiotics is one group of important pharmaceuticals in the veterinary medicine market. Discharge of antibiotics from wastewater treatment plants lead to their presence in river and groundwater. In agricultural regions, application of animal manure on crop lands is a major contamination path in the environmental matrices. Contamination by veterinary antibiotics should be managed with long-term perspectives.

Most of past studies focused on the detection and monitoring of the veterinary antibiotics in agricultural land and water bodies. However, the studies provided only little quantitative knowledge on transport and fluxes of pharmaceuticals in the agricultural soils. The main purpose of this study is to investigate the transport processes of veterinary sulfonamide antibiotics (Sulfadimethoxine, Sulfamethazine, and Sulfamethoxazole) in agricultural soils in Haean catchment located in South Korea. In particular, we emphasized in detail: i) sorption and transport of the sulfonamides in structured and homogeneous soil columns, ii) distribution of the applied antibiotics in runoff and soil layer on sloped fields, iii) comparing the transport processes between sulfadimethoxine and sorbable/unsorbable tracers.

In the batch sorption study, sorption of the all three sulfonamides was non-linear, and the Freundlich isotherm provided the best fits to the measured data. For all target sulfonamides, their sorbility to the soils decreased with increasing pH value of aqueous solutions in range of 4.0-8.0. An increasing sorption tendency was obtained in the following order: Sulfadimethoxine>Sulfamethoxazole> Sulfamethazine. Transport of the antibiotics in soils with different soil structures and pH conditions was quantitatively investigated with a numerical modelling program, HYDRUS-1D. The soil column studies using a conservative tracer, bromide and the antibiotics showed that an important transport mechanism in the natural soil columns can be preferential flow through macropore. A comparison of water flow and

solute transport in natural and disturbed soil columns revealed that the transport processes were affected by the soil structure. The transport of the sulfonamides was typical non-equilibrium process, and their mobility was reduced with decreasing pH value.

In the field campaigns, loss of the antibiotics varied between two sloped fields, and was related to the slope of the surface and precipitation. Heavy rainfalls during Monsoon season from 24 June, 2011 to 10. July, 2011 generated a huge amount of overland flow as well as seepage water in the soil layer. In accordance with the field measurements and modelling with HydroGeoSphere, water fluxes were higher for the more sloped site during the entire monsoon season. Among the sulfonamides, the mobility of sulfadimethoxine in the soil layers was relatively low. This reflects that the mobility of the sulfonamides was strongly dependent on their sorbility on soil materials.

In the tracer experiments with Brilliant Blue FCF, image analysis for horizontal cross-sections of the soil columns showed that dye coverage was almost 100% in the upper 6 cm. Below the fully dye covered depth, the ratio of dye coverage decreased more rapidly for disturbed soils due to their homogeneous soil structure. Both lateral and vertical dispersion of bromide were higher compared to Brilliant Blue FCF and sulfadimethoxine, which demand more time to reach flow regions than bromide. This reflects that water flow does not coincide with transport of the sorbable solutes, Brilliant Blue FCF and the sulfonamide due to adsorption to soil materials.

In summary, this thesis provided valuable knowledge about the transport phenomena of veterinary pharmaceuticals in agricultural soils. Through coupling of laboratory experiments, field campaigns and numerical modelling studies, major transport processes in soils can be quantitatively described. In this thesis, we present several recommendations, aiming at reducing the risk of pharmaceuticals in groundwater and surface water. In order to reduce

residual amounts of the contaminants in the environment, direct application of animal faeces and urine to agricultural lands should be restricted. Preferential flow in macropores leads to fast movement of contaminants to deeper soil layers, which results in a high risk of groundwater pollutions. We suggests regular ploughing in order to remove rest of roots creating preferential flow paths. One important sources of the antibiotics in surface waters is runoff and soil erosion from agricultural lands. To reduce their input into surface waters, we recommend establishing buffer zones between agricultural fields and streams

Zusammenfassung

Sulfonamidantibiotika werden in großen Mengen in der Medizin vermarktet. Über kommunale Abwässer und Kläranlagen gelangen sie in Oberflächengewässer und ins Grundwasser. Auch der Einsatz von Tierarzneimitteln in der landwirtschaftlichen Nutztierhaltung und Teichwirtschaft gilt als Mitverursacher von Arzneimittelrückständen in der Umwelt. Sulfonamidantibiotika gelangen üblicherweise mit der Gülle und dem Stallmist auf landwirtschaftliche Felder und können durch Abschwemmung in Oberflächengewässer bzw. durch Versickerung ins Grundwasser gelangen. Die Kontamination der Umwelt mit Arzneimittelrückständen ist aus der Sicht des nachhaltigen Umweltschutzes nicht akzeptabel.

Bisherige Studien fokussierten vor allem auf die Beschreibung des Vorkommens von Tierarzneimittelrückständen in landwirtschaftlichen Feldern und Gewässern. Diese Forschungen stellen jedoch nur wenige Ergebnisse bereit, aus denen quantitative Aussagen über Transportvorgänge abgeleitet werden können. Das Hauptziel dieser Doktorarbeit ist die Untersuchung von Transportprozessen ausgewählter Veterinärantibiotika der Sulfonamid-gruppe (Sulfadimethoxine, Sulfamethazine, Sulfamethoxazole) in Böden einer typischen landwirtschaftlichen Region im Haean Einzugsgebiet in Südkorea. Im Gegensatz zu bisherigen Forschungsarbeiten wurden Feldstudien mit numerischen Modellierungen und geeigneten Laborexperimenten, die die verschiedenen geohydraulischen Bedingungen in landwirtschaftlichen Böden mit Spurenstoffen beschreiben, kombiniert. Die Schwerpunkte dieser Arbeit können wie folgt beschrieben werden: i) die Beschreibung der Sorption und des Transports von Sulfonamiden in Bodensäulen mit verschiedenen Struktureigenschaften, ii) die Erfassung und Verteilung der Antibiotika in Oberflächenabfluss und den Bodenschichten in landwirtschaftlich genutzten Hängen während der Monsunzeit. iii) der Vergleich des Transportverhaltens von Sulfadimethoxin und sowohl sorbierbaren als auch nicht sorbierbaren

Tracer in Bodensäulen.

Die Sorption von 3 Sulfonamiden in den untersuchten Böden war bezüglich der Konzentration nicht-linear. Die ermittelten Messwerte wurden an verschiedene Gleichgewichtsisothermen nach der Methode der kleinsten Quadrate (least squares) angepasst. Die beste Anpassung wurde mit der Freundlich-Isotherme erzielt. Für alle auswählten Sulfonamide wurde bei pH-Werten zwischen 4.0 und 8.0 eine Zunahme der Sorption mit abnehmendem pH verzeichnet. Die Sorptionsfähigkeit war bei Sulfamethazine < Sulfamethoxazole < Sulfadimethoxine. Zur Modellierung des Transports von Antibiotika bei verschiedenen Bodenstrukturen und pH-Werten wurden mit Hilfe der Versuchsergebnisse die Parameter der Gleichgewichtsisothermen der Sulfonamide durch inverse Modellierung mit HYDRUS-1D ermittelt. Der Transport der Sulfonamide in den Bodensäulen aus koreanischen Feldern wird ferner durch hydraulische Parameter beeinflusst, die ebenfalls durch inverse Modellierung ermittelt wurden. Versuchsergebnisse mit Bromid (konservativer Tracer) und den Antibiotika zeigten, dass ein wichtiger Transportmechanismus im ungestörten Boden der präferenzielle Fluss entlang von Makroporen sein kann. Durch Unterschiede in der Porenstruktur bei natürlich gelagerten Böden und homogenen (gestörten) Böden ergibt sich eine Differenzierung des Transports von Sulfonamiden und Tracern. Der Transport aller Sulfonamide war durch ein Sorptionsgleichgewicht charakterisiert, das von pH-Werten deutlich beinflusst wurde.

In den Feldkampagnen variiert der Verlust durch Oberflächenabfluss und Sickerung der Antibiotika zwischen zwei Hängen als Folge der Hangneigung. Starkregenereignisse während der Monsunzeitraums führten vom 24. Juni, 2011 bis 10. Juli, 2011 zu einer Aufteilung des Niederschlags in Oberflächenabfluss und Infiltration. Abflussbildung und der hiermit verbundene Verlust an Sulfonamiden war abhängig von Regenintensität und Steigung. Die

Übereinstimmung von mit HydroGeoSphere ermittelten und gemessen Oberflächenabflüssen und Matrixpotentialen war akzeptabel. Die Stickwassermenge in den Versuchsfeldern wurde ausschließlich über Modellierung mit HydroGeoSphere ermittelt. Die Sickerwassermenge und der hiermit verbundene Austrag an Sulfonamiden aus Feld B war höher als Feld A. Da die Sulfadimethoxine relativ stark an die Bodenpartikeln sorbiert werden, gibt es insgesamt eine geringe Desorption und geringe Auswaschung aus dem Boden. Bezüglich der Mobilität von Sulfadimethoxin wurde somit eine langsame Verlagerung entlang der Fließstrecke im Boden festgestellt.

Die Ergebnisse der Bildanalyse für horizontale Bodenabschnitte in den Tracer-Experimente zeigten, dass fast 100% der Oberflächen bei den ungestörten und gestörten Bodensäulen gefärbt waren. Bei den gestörten Böden reduzierte sich der Anteil an gefärbten Bereichen aufgrund des deutlich geringeren Makroporenanteils mit zunehmender Tiefe. Die vertikalen Verläufe der Bromidkonzentrationen in gestörten und ungestörten Böden zeigten ein langes ”Tailing“ aufgrund der intensiven lokalen Durchmischung. Im Gegensatz zum konservativen Tracer blieben Sulfadimethoxine und Brilliant Blue FCF weitgehend in den oberen Bereichen der untersuchten Säulen. Die horizontale Ausbreitung des Farbstoffs und des Antibiotikums wurden in den untersten 9 cm des Bodenprofils eingeschränkt. Insgesamt lässt sich feststellen, dass aufgrund der hohen Sorption die horizontale und vertikale Dispersion von Sulfadimethoxine und Brilliant Blue FCF gering war, obwohl eine relative hohe laterale Ausbreitung von Bodenwasser beobachtet werden konnte.

Zusammenfassend konnte die Arbeit wertvolle neue Erkenntnisse über das Transportverhalten ausgewählter Veterinärantibiotika in landwirtschaftlichen Böden liefern. Durch die Kopplung von Laborexperimenten und Feldkampagnen mit nummerischen Modellstudien konnten Haupttransportprozesse in Böden beschrieben werden. Basierend auf

den vorliegenden Ergebnissen werden in dieser Arbeit mehrere Vorschläge gemacht, um die Gefährdung und Belastungen in Grund- und Oberfläschengewässern durch Pharmaka zu vermindern. Um Einsatzmengen der Schadstoffe in der Umwelt zu reduzieren, sollte das direkte Ausbringen der Gülle und Stallmist auf Agrar- und Weideländern verboten werden. Der präferentielle Fluss in Makroporen kann das Risiko einer Grundwasserkontamination verstärken. Daher empfiehlt es sich regelmäßiges Pflügen zur Bodenvorbereitung, um den Restbewuchs des vorhergehenden Anbaus zu entfernen. Ein wichtiger Eintrag von Antibiotika in Fließgewässer ist der Transport von Bodenpartikeln aus landwirtschaftlichen Flächen über den Oberflächenabfluss. Daher empfehlen wir, Pufferzonen zwischen landwirtschaftlichen Flächen und Fließgewässern einzurichten, um damit den direkten Eintrag von Antibiotika zu reduzieren.

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LIST OF ABBREVIATIONS

Ap	ploughed topsoil horizon
Bw	subsoil horizon
Bwb	subsoil horizon with buried soil
BB	Brilliant Blue FCF
Br	bromide
Cl^-	chloride ion
FDR	frequency domain reflectometry
EDTA	ethylenediaminetetraacetic acid
HPLC-MS-MS	high-performance liquid chromatography with tandem mass spectrometry
KBr	potassium bromide
MAE	mean absolute error
NSE	Nash-Sutcliffe coefficient
R	Pearson's correlation coefficient
R^2	coefficient of determination
RMSE	root mean square error
USDA	United States Department of Agriculture

LIST OF SYMBOLS

Symbol	Definition	Dimension
α	inverse of the air entry suction	$[L^{-1}]$
C_e	equilibrium concentration	$[M\ L^{-3}]$
C_{mo}	concentrations of solute in the mobile region	$[M\ L^{-3}]$
C_{mo}	concentrations of solute in the immobile region	$[M\ L^{-3}]$
D	longitudinal dispersivity	[L]
D_f	free-solution diffusion coefficient for the matrix	$[L^2\ T^{-1}]$
f	sink term	$[M\ L^{-3}\ T^{-1}]$
Γ_w	mass transfer rate for water from immobile region and mobile region	$[M\ L^{-3}\ T^{-1}]$
h	pressure head	[L]
λ	degradation coefficient	$[L^{-1}]$
K_d	linear adsorption coefficient	$[L^{-3}\ M]$
K_f	Freundlich adsorption coefficient	$[L^{-3}\ M]$
K_s	hydraulic conductivity	$[L\ T^{-1}]$
l_{ex}	coupling length	[L]
μ	degradation coefficient	$[L^{-1}]$
n	measure of the pore-size distribution	[-]
q	subsurface water flux	$[L\ T^{-1}]$
q_e	amount of adsorbate in the adsorbent at equilibrium	[-]
τ	matrix tortuosity	[-]
θ_{mo}	residual water content in mobile zone	[-]
θ_{im}	saturated water content in immobile zone	[-]
θr	residual water content	[-]
θs	saturated water content	[-]
ν	pore-water velocity	$[L\ T^{-1}]$
z	elevation head	[L]
Ω_{ex}	mass exchange rate of solute between subsurface and surface domain	$[M\ L^{-3}\ T^{-1}]$
1/n	adsorption intensity	[-]

Chapter 1

General introduction

1.1 Occurrence and origin of veterinary antibiotics in environment

Veterinary pharmaceuticals are widely used in commercial animal farming in order to control diseases and to increase productivity. Application of the medical compounds to animals can bring about dispersion of the medical active materials in environment. Owing to toxicological issues of pharmaceuticals in environmental matrices, several studies concerning veterinary pharmaceuticals have been conducted in USA and Europe since 1990s. Some toxicological researches have shown that the concentration as low as in the several μg/L level may cause physiological damages to terrestrial and aquatic organisms (Huang et al., 2014; Kim et al., 2007). Nevertheless, understandings of the organic compounds are limited to prove toxicological concerns for terrestrial and aquatic ecosystem.

Demand of antibiotics used for animal production is huge in veterinary medicine market of developed countries. In Korea, the amount of purchased veterinary antibiotics was about 1600 tons in 2001 (Korea Food and Drug Administration, 2006), and 700 tons of the antibiotics were consumed in United Kingdom in 2004 (Veterinary Medicines Directorate, 2005). Various kinds of veterinary antibiotics are not fully adsorbed into animal body, and the rest of active compounds are excreted through manure and urine. Applying of manure as fertilizer is a highly relevant exposure route in agricultural regions. Existence levels of these compounds are dependent on concentration of antibiotics in manure, amount of manure application, type of environmental matrices, and characteristics of antibiotics. Previous studies have been reported that concentrations of the antibiotics are up to several mg/kg in soil.

Through infiltration and surface runoff, the antibiotics finally reach the subsurface soil and ground water as well as surface water.

As reported by USDA, the annual amount of manure production was about 335 million tons (USDA-ARS, 2005). Concentration of the antibiotics in manure ranged from 1 to 10 mg, and recorded up to 200 mg/kg. Compared to other medical active substances, the antibiotics are strongly resistant to degradation by microorganisms. This implies that the antibiotics are persistent in soil, and consequently can induce chronic effects on terrestrial and aquatic organisms.

1.2 Significance of veterinary sulfonamide antibiotics for environmental and ecotoxicological issues

Representative veterinary sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine) in EU and Korean medical market were chosen for this research. The demand of whole veterinary antibiotics admitted in Korea was estimated to be about 1000 ton per year, and approximately 100 tons of the antibiotics were used as feed additive (Korea Animal and Plant Quarantine Agency, 2012). Consumption of sulfonamide antibiotics was ca. 100 ton in Korea. In the United Kingdom, 700 tons of the antibiotics were purchased in 2004 (Veterinary Medicines Directorate, 2005). 1000 tons were consumed in France in 2010, and the amount of the sulfonamides antibiotics accounted for 17 percent of whole consumption (European medicines agency, 2012).

Sulfonamides have been generally consumed in animal farming for therapeutic purposes, in order to control various infectious diseases (Grant et al., 2003; European medicines agency, 2012). In particular, a huge amount of sulfonamide antibiotics was used for swine production. For pigs and sheep, sulfonamide antibiotics have been consumed to cure several diseases occurred by E. streptococcal and brucellosis (Giguère et al., 2007). In several countries (e.g. Korea and USA), some of sulfonamide antibiotics are registered for cattle and swine production as nontherapeutical agent. It implies that sulfonamide antibiotics are used as feed additive and can be obtained without prescription for productivity of animals.

Concerns with exposure of the sulfonamides and their metabolites cover reproductive malfunction, carcinogenicity, abnormal physiological development and increase of resistance against the antibiotic substances (Wollenberger et al., 2004; Froehner et al., 2000; Migliore et al., 1993; Kilkkinen et al., 2008). Report on phytotoxicity to crops (e.g. corn and pea) has revealed that sulfonamide antibiotics may inhibit the growth of leaves and roots at several hundred mg/L (Migliore et al., 1995; Jjemba, 2002). Research conducted by National Center for Toxicological Research has shown that thyroidal tumor in rats is strongly related to high oral dose of sulfamethazine (Littlefield et al., 1990).

In agricultural lands, the Pharmaceuticals can be taken up into plants via soil pore water. For example, uptake of sulfamethazine by crops (e.g. lettuce, potato and corn) has been reported, in range from 0.1 to 1.2mg/kg dry weight (Dolliver et al., 2007). Nevertheless, the accumulation rate of sulfonamide antibiotics in plant was less than 0.1% of total applied amount in soil (Boxall et al., 2006). Even though bioaccumulation of the antibiotics is low in plants, exposure via the plant materials consumed in the diet can physiologically cause negative effects on human body, due to low acceptable daily intake (ADI) of the veterinary antibiotics (Boxall et al., 2006).

Biodegradation of sulfonamide antibiotics spread on soil is fairly slow. A laboratory study reported that degradation of sulfonamide antibiotics in soil may be affected by soil properties and temperature, pH (Boxall et al., 2003). Applying of manure in soil can increase the degradation rates of sulfonamide group, owing to additional microbial activity and supply of nutrient derived from manure (Wang et al., 2006; Accinelli et al., 2007). A previous study showed that degradation of sulfadimethoxine in manure-amended soil is related to concentration of the sulfonamide. Sulfadimethoxine degradation was faster, as increasing moisture in soil (Wang et al., 2006). The degradation of sulfadimethoxine was accelerated under aerobic conditions compared with anaerobic condition (Wang and Yates, 2008; Liu et al., 2010). The degradation of sulfadiazine in surface water is slightly affected by oxidation-reduction condition (Ingerslev et al., 2001). Degradation can reduce toxicological potentials of sulfonamides. But several metabolites have similar toxicity to their parent substance (Halling-Sørensen et al., 2002). Conjugation involved in degradation pathways generally enhances water solubility of daughter compounds. The transformation reaction of sulfonamide antibiotics by microorganisms is known to be demethylation in sediments (Samuelsen et al., 1994). Although degradation processes can increase mobility of antibiotics in soil, the degradation processes may lead to substances with higher toxicity than that of the mother compounds (Halling-Sørensen et al., 1998).

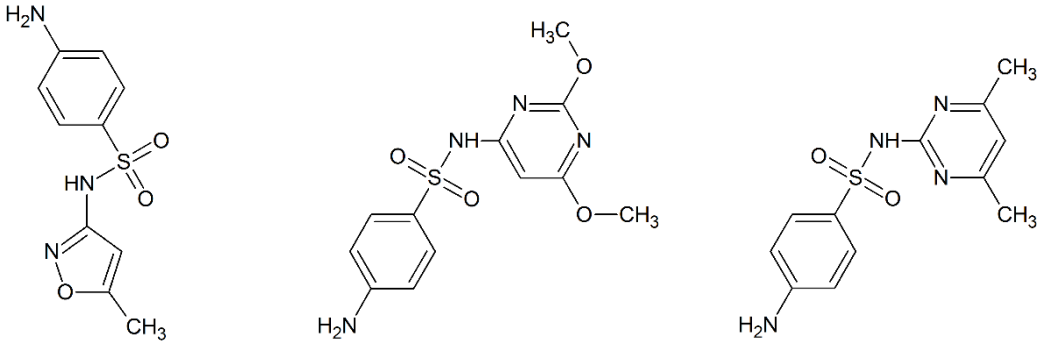
Owing to toxicological concerns and resistance against microorganisms, fate and transport of the sulfonamide antibiotics have recently been of interest to assess toxicological risk in environmental matrices. Fate and distribution of the sulfonamide group in environment is affected by reactions between sulfonamides and soil-water interface (Boxall et al., 2002; Thiele-Bruhn and Aust, 2004; Gao and Pedersen, 2005). In accordance with several studies, mobility of sulfonamide antibiotics is associated with sorption onto soil particles (Accinelli et

al., 2007). Sorption potential of sulfonamide group is dependent on pH of soil, due to conversion of deprotonated form from cationic sulfonamides (Boxall et al., 2002; Thiele-Bruhn and Aust, 2004). As increasing pH of soil, deprotonated species resulting in high sorption are dominant. Sorption of protonated sulfonamides is generally observed at negative surface of clay minerals.

In order to expend knowledge on the risk posed by the sulfonamide antibiotics, it is required to understand the hydrological and chemical parameters that affect movement of these antibiotics in soil-water interface. So far, transport and fate of the pharmaceuticals is not fully understood. For the sake of reducing potential adverse effect caused by the veterinary antibiotics, transport phenomena of representative antibiotics in medical market should be clearly described in detail.

1.3 Property of target sulfonamide antibiotics

Sulfonamide is an organic sulfur compound containing the amides of sulfonic acid (-SO_2NH_2), as presented in Fig. 1.1. The molecular structure is similar to p-Aminobenzoic acid (PABA) required to bacteria as a substrate of the enzyme (dihydropteroate synthetase) for synthesis of tetrahydrofolic acid (THF). Sulfonamide antibiotics are derived from sulfanilamide synthesized from acetanilide. They can interrupt the metabolic process in bacteria that needs PABA. They act as antimicrobial agents by inhibiting bacterial growth and activity. Since Prontosil, first sulfonamide antibiotics has been introduced in 1930s, they are used in the prevention and treatment of bacterial infections, diabetes mellitus, edema, and hypertension. The properties of sulfamethoxazole, sulfadimethoxine and sulfamethazine are given in Table 1.1.



<Sulfamethoxazole> <Sulfadimethoxine> <Sulfamethazine>

Fig. 1.1 Structure of sulfamethoxazole, sulfadimethoxine and sulfamethazine

Table 1.1 Properties of sulfamethoxazole, sulfadimethoxine and sulfamethazine

Compound	Formula	Ka	Kow[(b)]	Solubility(pH 7.0)[(a)]
sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	1.8[(c)], 6.0[(d)]	8	1900
sulfadimethoxine	$C_{12}H_{14}N_4O_4S$	1.9[(e)], 6.1[(d)]	40	260
sulfamethazine	$C_{12}H_{14}N_4O_2S$	2.4[(c)], 7.4[(d)]	2	7000

[(a)]Schönfeld (1987), [(b)]Hansch (1995), [(c)]Lin et al. (1997), [(d)]Neumann (1981), [(e)]Petz (1986)

Sulfonamide antibiotics are typical weak-acid and moderately water-soluble compound. The antibacterial activity of sulfonamides relies on their lipophilicity, which determines their ability to penetrate inside the bacteria and their ionization in water. Substitution group of the sulfonamide antibiotics can modify physico-chemical properties, such as pK_a and water solubility, as given in Table 1.1.

1.4 Overview of this thesis

1.4.1 Study area

The Haean catchment is located in the North-eastern part of Gangwon Province in South Korea, about 2km from the border to North Korea. The whole area of the catchment is about 62km^2, and is divided into three land use zone. Dryland farming is dominant in the hillsloped parts of the catchment, while rice cultivation is mostly practiced in the flat agricultural areas. The average precipitation is estimated as 1500 mm/yr, and 50-60 % of total annual precipitation is concentrated in summer monsoon from June to July. However, frequency and amount of rainfall increased from late July to mid-August, because withdrawal time for Changma has tended to be late in the recent decade (Ha et al., 2005).

The steep farmlands surrounding mountainous ridges are mainly covered with acidic and podzolic Cambisols formed from weathered metamorphic rock (Meusburger et. al, 2013). Due to high soil erosion caused by runoff generation during summer monsoon season, artificial additions of sandy soil are frequently used in order to compensate the soil loss. Therefore, the agricultural land management is strongly relevant to the fast pollutant leaching from top soil to adjacent soil horizons.

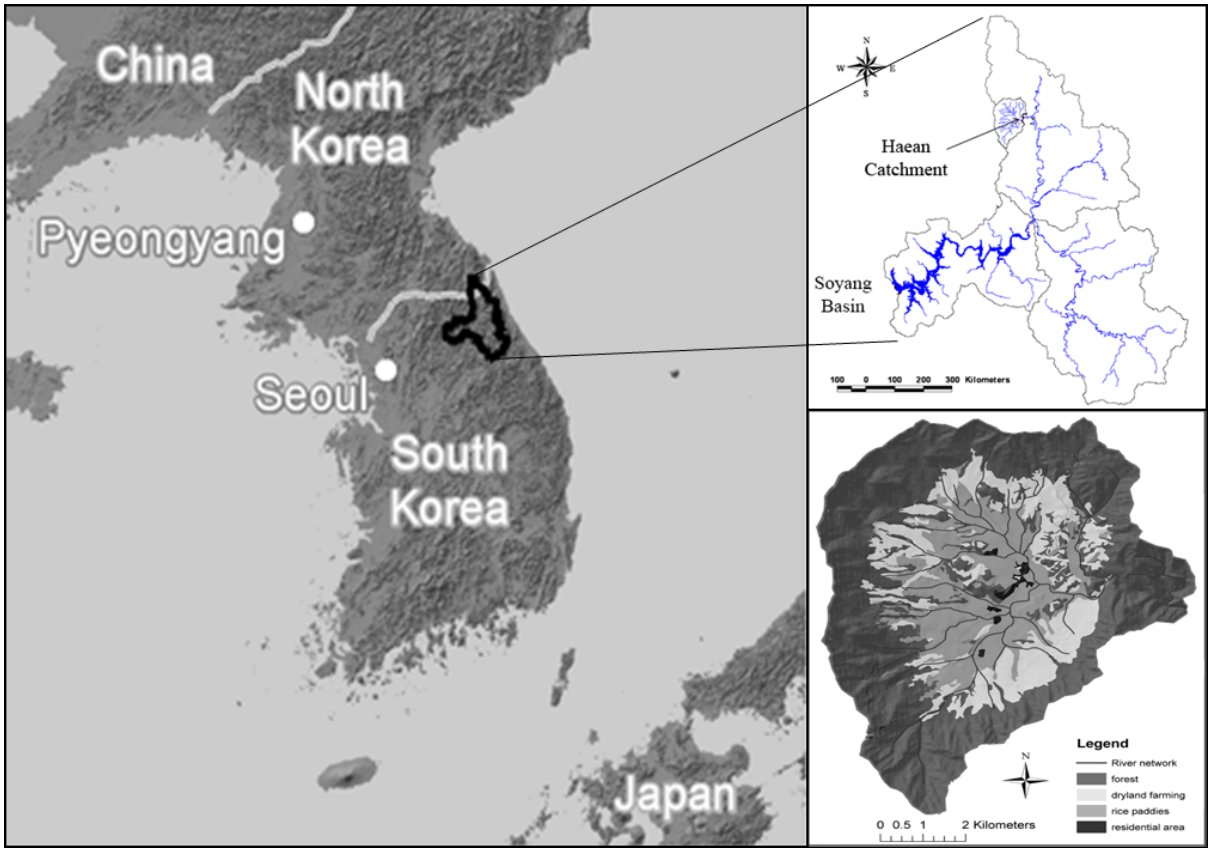


Fig 1.2 Map of South Korea (left), location of Haean catchment in Soyang Basin (top right), land use map of Haean catchment (bottom right).

In order to investigate transport processes of the target sulfonamide antibiotics in agricultural soils, we performed soil column experiments under different pH conditions (chapter 2). Field experiments were conducted on two sloped crop fields during summer monsoon season (chapter 3). Dye tracer experiments were carried out with undisturbed and disturbed soil columns taken from Haean catchment (chapter 4).

1.4.2 Objectives and hypotheses

The main objective of this study is to depict transport and fate of selected sulfonamide antibiotics in soil, using antibiotics with laboratory and field experiments as well as with modelling programs. In the first part of this thesis, we studied the transport of chosen

sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine) in soil columns which have different soil structure. The second study focused on transport of applied antibiotics in agricultural land during rainy season, called monsoon. In the last study, we tried to visualize transport paths of the sulfonamides using Brilliant blue FCF.

Study 1: Effect of soil structure and pH on transport of sulfonamide antibiotics

Transport of contaminants in soil has been studied in several researches. According to studies by Ghodrati et al. (1992) and Bundt et al. (2000), presence of various pollutants in deep soil layer and groundwater is strongly associated with rapid flow caused by heterogeneity of soil structure. Preferential flow refers to the rapid movement of water and solutes through macropores, such as cracks, root holes and wormholes. On the contrary of preferential flow, matrix flow is relatively slower water movement through finer pores in soil. Sorption between solutes and soil materials affects their mobility in vadose zone (Curtis et al., 1986; McCarthy and Zachara, 1989). For acidic organic compound, pH of soil and water can influence on sorbility and sorption capacity (Calvet, 1989; Delle Site, 2001). In order to describe transport and behavior of the sulfonamide antibiotics in soil-water interface, the influence of pH on sorption should be well understood, since sulfonamide antibiotics are typical acidic compounds in aqueous phase.

The aims of this study were to show effects of soil structure and pH on the transport of chosen sulfonamide. Our hypotheses in this study are as listed below;

- The heterogeneity of soil structure is responsible for rapid transport of the sulfonamides in soil column.

- Increasing pH of aqueous solution enhances mobility of the chosen sulfonamide antibiotics in soil.

- Adsorption of the sulfonamide antibiotics onto soil materials is determined by pH changes in aqueous solution.

For the above hypothesis, we conducted batch sorption experiments with agricultural soils having different soil properties. In order to prove effects of pH changes and soil structure on transport of the sulfonamides, we analyzed transport patterns in soil columns.

Study 2: Transport of sulfonamide antibiotics in crop fields during monsoon season

Precipitation-driven transport of organic pollutants is an important transport mechanism in agricultural region. During the rainy season, pesticides can be rapidly redistributed in watershed and agricultural land (Guo et al., 2004). The monsoon rains may move the containments emitted in the crop fields to the watershed, including rivers and lakes. Up to date, transport and distribution of sulfonamide antibiotics in agricultural areas have not been investigated during the rainy season. Objective of this study was to describe transport of the selected veterinary sulfonamides in small agricultural field. For this study, we measured sulfonamide antibiotics and the conservative tracer, bromide in soil-water and runoff. As modelling tool, HydroGeoSphere was used in order to simulate the transport phenomena in subsurface, as well as at surface region. For this research, we set up the following hypotheses:

- Heavy rain events lead to rapid transport of the applied sulfonamide antibiotics in crop fields.

- Transport of sulfadimethoxine is retarded in subsurface soil, due to relatively high adsorption onto soil.

- Increasing slope of the crop fields reduces mobility of the sulfonamides in subsurface region, owing to higher runoff generation.

Study 3: Sulfadimethoxine transport in soil columns in relation to sorbable and nonsorbable tracers

Various types of contaminants have been frequently detected at deeper soil layers than expected from their properties (Flury, 1996). Rapid transport has been observed, when the fast transport pathways (e.g. earthworm burrows, cracks and roots) was developed in soil layer (Flury, 1996). The development of preferential flow pathways is affected by soil management, soil characteristics and climate (Gerke, 2006). The fast water flow may lead to non-equilibrium transport, and consequently enhances mobility of the organic pollutants in soil, compared to matrix flow. For organic pollutants, sorption strength correlates strongly to transport velocity of the compounds in soil-water interfaces. For example, Kladivko et al. (1999) demonstrated that movement of atrazine was relatively slower than carbofuran in agricultural land, owing to higher K_d value of atrazine.

So far, several dye substances have been used to visualize transport pathways of water in vadose zone. Brilliant Blue FCF is a representative dye to show flow path in soil, and it is generally applied at the soil surface. Bogner et al. (2008) pointed out that the stained pattern can be affected by adsorption strength of applied dyes. Brilliant Blue FCF is considered as a chemical, moderately adsorbing at particle surfaces of soils, and may be a proper tracer to show transport pathway of adsorbable compounds.

In a transport study with agro-chemicals, Reichenberger et al. (2002) proved that high adsorbable pesticides tend to be transported by preferential flow. This research confirmed that the Brilliant Blue FCF is able to visualize the transport pathways of applied pesticides. Consequently, Brilliant Blue FCF can be an effective dye for selection of sampling points (Gjettermann et al., 2011).

Up to date, transport pathways of pharmaceuticals have not been investigated using dye tracers. The purpose of this study is to visualize sulfadimethoxine transport paths in soil with Brilliant Blue FCF. Distribution of the target antibiotics and tracers was also identified in disturbed and undisturbed soil columns with digital image processing and chemical analysis. For this research, we formulated the following hypotheses:

- Brilliant Blue FCF can be used to effectively visualize pathways of sulfadimethoxine in soil column.

- Heterogeneity of soil in soil columns affects transport pathways and patterns of sulfadimethoxine and Brilliant Blue FCF

1.4.3 Methods and results

1.4.3.1 Effect of soil structure and pH on transport of sulfonamide antibiotics

The presence of trace levels of sulfonamide antibiotics in the environmental system has concerned developed regions as well as international organizations. For acidic antibiotics, transport studies are rare in literature under different pH condition and soil structures, although the majority of studies have attested the general presence of sulfonamides in soils from ng/L up to μg/L level. We aimed to evaluate the effect of soil structure and pH on transport of the

target sulfonamide antibiotics.

Soil columns were taken in Haean catchment located at north-east of Gangwon province, South Korea (soil A: N 38° 16', E 128° 8', soil B: N 38° 14', E 128° 7'). For batch sorption experiments of the sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine), soils were taken from an agricultural region in Yanggu, Korea. Three replicate tubes (glass with Teflon liner screw cap, D: 20mm, L: 100mm) were prepared for each treatment by adding 2g of dry soil and 10ml of working solution (pH 4.0-8.0) containing 0.01M KBr to pre-weighed tubes. The mixtures were homogenized with a shaker at room temperature for 24 hours. At the end of the contact time, the antibiotics remaining in the aqueous aliquot was determined with HPLC-MS-MS.

For column experiment, undisturbed and disturbed soil columns (D: 15cm, L: 30 cm) were collected from the same agricultural region. After wetting with deionized water, aqueous solutions (pH 4.0-8.0) with each sulfonamide antibiotic (1mg/L) and KBr (1g/L) were applied to disturbed and undisturbed soil columns with a peristaltic pump at 5.6m/min. Leachate from each soil column was collected every 5 minute. Residual concentration of the sulfonamides and conservative tracer, bromide in the leachate was determined with HPLC-MS-MS and ion-selective electrode in combination with reference electrode. HYDRUS-1D was used to depict solute transport and water flow in the soil columns.

Sulfamethazine, sulfamethoxazole and sulfadimethoxine were weakly adsorbed onto both soils taken from the agricultural region. |In range from pH 4.0 to 8.0, adsorption of sulfonamide antibiotics showed a clear relationship to pH. Sulfadimethoxine had higher adsorption coefficient (K_d) value than other sulfonamides under weak acid and neutral condition (pH 4.0-7.0). Adsorption of sulfamethoxazole and sulfadimethoxine were also pH-dependent reactions, but relatively less sensitive to pH compared to sulfadimethoxine. The pH-

dependent sorption was caused by their acid-base properties in aqueous solution. The sorption reaction corresponds to the changes in the fraction of ionized sulfonamide antibiotics, since the sulfonamide antibiotics transform from their cationic species to neutral and anionic species with increasing pH. Positive- and neutral-charged forms can electrostatically bound to negative-charged surfaces of soil minerals. Consequently, lower K_d and K_f values were estimated at higher pH.

Bromide breakthrough curves for undisturbed soil columns had earlier arrival times and peak times than those observed in disturbed soil columns. This proves a well-developed macropore network in all undisturbed soil columns. The bromide breakthrough curves were fitted to similar shape in both of undisturbed and disturbed soil column. Since bromide is a nonreactive tracer and is simultaneously transported with water flow, breakthrough curve and hydraulic parameter estimation with Hydrus-1D shows that bromide transport was a typical convection-dispersion process without sorption and degradation.

The hydraulic conductivity and longitudinal dispersivity estimated by inverse modelling revealed that the water flow and the sulfonamide transport in disturbed soil was slower than in undisturbed soil. Soil disturbance destroys the macropore network in disturbed soil columns, and therefore matrix flow was dominant in disturbed soil columns. The elimination of the coarse particles and macropore channels caused relatively lower hydraulic conductivity and longitudinal dispersivity in disturbed soil column.

Column experiments for sulfonamide antibiotics were performed at different pH values. With increasing pH values in the solution, peak concentrations of the sulfonamides in leachate were increased, regardless of the soil origin and homogeneity. Relatively higher retention time in disturbed soil columns assures that the antibiotics are closer to sorption equilibrium. Under this condition, effect of pH was apparently more revealed, compared to undisturbed soil

columns where faster water flow was observed. For both undisturbed and disturbed soil column, sulfonamide breakthrough curves were asymmetric. They had tailings for desorption phase, indicating that nonequilibrium adsorption occurred between the sulfonamides and soil materials. Transport of sulfadimethoxine in soil column was the most sensitive to pH among the chosen antibiotics. The effect of pH on sulfonamide transport were correlated with their pK_a and isoelectric points (sulfadimethoxine: 4.0, sulfamethoxazole: 3.9, sulfamethazine: 4.9). Blow isoelectric point, positive and neutral form of sulfonamide was dominant in aqueous solution. Surface of soil mineral is generally negatively charged, and electrostatical interaction can be easily induced between soil and the non-positive form. At same pH, partitioning of the sulfonamide antibiotics was therefore affected by abundance of non-positive species determined by the substitution group. This is consistent with findings of our batch sorption experiments and previous studies (Avisar et al., 2010).

The adsorption behaviour was a pH-dependent reaction, which is an important factor for interpretation of transport and fate of the veterinary antibiotics in soil-water system. Among the testing sulfonamides, sulfadimethoxine has the highest adsorption affinity, and the adsorption phenomena are strongly affected by the pH value.

Transport velocity of the applied sulfonamides into undisturbed column were relatively fast, compared to homogeneous column. Modelling with HYDRUS-1D showed that soil structure and heterogeneity which are attributed to hydraulic parameters determined the movement of the antibiotics in the soil system. In this study, it was proven that transport of the sulfonamides is pH-dependent in the soil system, and pH should be considered to describe fate and transport of the sulfonamides in soil-water matrices, as well as soil properties and structure.

Our findings can be transferred to additional studies focusing on transport process of other acidic organic pollutants in the soil-water interface. The target antibiotics dissolved in

water were applied for our column experiment. In general, they put into agricultural region in form of manure mixture or compost. Natural organic matter can affect mobility of the sulfonamides in environmental matrices. Therefore, their effect on sulfonamide transport should be considered in both laboratory and field-scale researches.

1.4.3.2 Transport of sulfonamide antibiotics in crop fields during monsoon season

During the rainy season, trace contaminants can rapidly move to the water body from agricultural land. Up to date, transport processes of veterinary sulfonamide antibiotics in agricultural area have not been studied during rainy season, such as summer monsoon. Therefore, we investigated the transport processes in combination with field measurement and modelling.

The field experiments were performed on agricultural fields (Rectangle, L: 8m, W: 2m) located at slope area in Haean catchment (N 38° 16', E 128° 8'; altitude 620 m). In this research, 100mg sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine) and 500g KBr were applied at each field on 20 May, 2011. The amount of precipitation from May to July were measured with an automatic weather station. TDR sensors and tensiometers were installed in two different sloped fields (Field A: 9.0°, Field B: 4.5°). Below 2 furrows and 3 ridges of each field, the measurement devices and suction candles were set up in depths of 20, 40 and 70 cm from surface of the furrows and ridges. Multislot divisors and pressure sensors were used in order to estimate runoff generation.

A hydrological simulation model, HydroGeoSphere was used in order to quantify water and the chosen solute transport. Initial hydraulic parameters of Van Genuchten equation were obtained using Rosetta Lite (version 1.1) based on soil texture. The lateral boundary was set to

zero-flux boundary due to block panels inserted around subsurface region. Volatilization was ignored, and the initial degradation rate was obtained from a previous study (Radke et al., 2009). Hydraulic and solute transport parameters were optimized by Parallel-PEST, which repeats determination of the parameter upgrade vector with further parameters held fixed (Doherty, 2004).

From 24 June, several strong rain events were observed up to 126mm/day, and the intensity of the precipitations were fluctuated. Runoff generation relied on rain intensity for whole experiment period. Slope of the experiment fields also affected runoff events. Compared to Field B, runoff generation from Field A was more frequently observed, and also the amount of runoff generation was relatively high (Field A: 0 – 84.18 L/hr, Field B: 0 – 70.42 L/hr).

Concentrations of the antibiotics and Br in runoff varied between two fields, depending on runoff generation and slope of the observed fields. After starting intensive precipitation on 23 June, bromide was detected in very low levels. Due to very low sorbility, the conservative tracer was rapidly transported into the subsurface layer and runoff at beginning of the rainy season. Concentrations of the antibiotics decreased during the strong precipitation like bromide. But the gradient of the antibiotics concentration was relatively low, compared to bromide. The difference may be caused by higher sorbility of the sulfonamide antibiotics to soil. Concentrations of the antibiotic in runoff were slightly different among the applied sulfonamide in the whole experiment, except in first runoff generation on 31 May. In the present study, slope of the fields effected on transport of the sulfonamide antibiotics and bromide by runoff. Simulation of the antibiotics transport showed a good agreement with measured values, although the transport model underestimated washout of the applied sulfonamides by runoff.

Two rain events that occurred before monsoon season also transported bromide from

the top layer into deeper subsurface region. During monsoon season, distribution of the bromide was dramatically changed in subsurface, and rapidly moved into deeper soil layer. Compared to the conservative tracer, transport of the sulfonamide antibiotics was relatively retarded in soil during the entire experiment period. Most amount of the applied antibiotics remained in the upper soil layer (≤ 10cm) during the dry season. After starting the rainy season, the applied antibiotics were rapidly moved into the subsurface region. In accordance with the modelling, the high water infiltration drove fast transport of antibiotics into deeper subsurface region during both dry and monsoon season. The results obtained from modelling and chemical analysis point out that distribution and transport of the sulfonamide antibiotics in subsurface is dependent on their sorbility.

The topological characteristics caused different pressure heads between ridge and furrow area. Although pressure head gradient was vertically higher at both fields (Field A: -7 cm to -316 cm, Field B: -3 cm to -319 cm), the horizontal gradient (Field A: -20 cm to -120 cm, Field B: -10 cm to -160 cm) partially caused soil water to move from ridge to furrow. Consequently, the ridge-furrow system was responsible for the different distribution of sulfonamide antibiotics. Slope of the fields also effected on distribution of the sulfonamide antibiotics in subsurface region. For distribution of the sulfonamide antibiotics in subsurface, no significant difference was observed between the fields before monsoon season. The difference in the residual concentration of the all sulfonamides between the fields became apparent below 70 cm depth during monsoon season.

In this study, we performed field measurements and modelling with HydroGeoSphere to investigate transport behaviour of the sulfonamide antibiotics and bromide during dry and monsoon season. High sloped area generated easily runoff, since partitioning of precipitation into subsurface flow decreased with increasing slope. This leads to higher loss of the

sulfonamide antibiotics and bromide by runoff under the rainy season. The model has a good agreement with measured concentration of the sulfonamide antibiotics in runoff, whereas outflow of the sulfonamide antibiotics induced by first rain events was underestimated.

At both experiment fields, the applied sulfonamide antibiotics was rapidly transported into the subsurface region during monsoon season. Before the rainy period, the most amount of the sulfonamide antibiotics remained within the topsoil layer (<20 cm depth), while the non-adsorbable tracer, bromide penetrated fast into the subsurface. Due to lower water infiltration caused by a higher slope gradient, all applied sulfonamide antibiotics and bromide in the more sloped area, Field A was transported faster into the deeper soil layer than in Field B. Our simulation properly described the distribution of the sulfonamides and bromide in subsurface, although their transport was underestimated during monsoon season, due to the existence of preferential flow. Recently, several studies point out various ecotoxicological problems associated with sulfonamides in the environment. The understandings and characteristics of sulfonamide transport need to be incorporated into other hydrological models to describe their toxicological issues at catchment and watershed level.

1.4.3.3 Sulfadimethoxine transport in soil columns in relation to sorbable and nonsorbable tracers

For organic pollutants, sorbility is strongly related to their mobility of the compounds in soil-water interfaces. A transport study by Reichenberger et al. (2002) offered that high adsorbable agro-chemicals tend to be transported in preferential flow paths. This research confirmed that the Brilliant Blue FCF visualized the transport pathways of applied pesticides. In our study, we identified the distribution of the target antibiotics, sorbable and nonsorbable

tracers in disturbed and undisturbed soil columns with digital image processing and chemical analysis.

For column experiment, soils were taken from typical agricultural fields consisting of sandy-loam soil in Haean catchment located in Gangwon Province, South Korea (Soil C: 38.2°N, 128.13°E, Soil D: 38.2°N, 128.12°E). In this study, we used undisturbed and disturbed soil columns with 30cm length and 15cm diameter. In order to estimate hydraulic parameters, 0.1M NaCl solution and deionized water was sequentially applied to soil column for 24hr. At the end of test for chloride breakthrough curve, aqueous solutions with sulfadimethoxine (25mg/L), Brilliant blue FCF (1g/L) and KBr (20g/L as Br) were sprayed to disturbed and undisturbed soil columns for 4hr at 5.6ml/min. Residual concentration of the sulfonamide and tracers were measured with HPLC-MS-MS, spectrophotometer and ion electrode. HYDRUS-1D was chosen for the sake of simulating water flow and estimating hydraulic parameters in soil columns.

To investigate the solute flow patterns, soil columns were horizontally cut at every 1.5cm depth intervals after column experiment. The cutting surfaces were photographed with a digital camera. In order to estimate the dye coverage of horizontal cutting images, we followed conditional dilation method (Serra, 1998).

For each soil column, the hydraulic parameters was estimated through inverse modelling based on Cl^- tracer experiments and the dual porosity model in Hydrus 1-D. Soil disturbance effected on hydraulic conductivity, ranging from 1.17 to 1.31 times higher than that in undisturbed columns.

Depth profiles illustrate that sulfadimethoxine and BB was leached relatively slow into the soil column, compared to Br. The antibiotic was concentrated only in stained area,

regardless of the soil origins and structures. For both undisturbed and disturbed soil D, no antibiotics were detected below each 25cm and 20cm depth, although the existence of brilliant blue FCF and dye covered area was observed in soil slices. The concentration of sulfadimethoxine in stained areas was 7-30 times higher than in unstained areas. In contrast, the bromide distribution was more homogeneous than sulfadimethoxine in all horizontal cross-sections. This reveals that the non-adsorbable tracer spread more in lateral direction without any reactions, compared to the sulfonamide and BB.

The overall mass recovery, which is the sum of residual ratio in soils and in leachate, was over 95% for all compounds, as short precipitation time (4hr) restrained biodegradation for the antibiotics and the organic tracer on soil columns. Br was also hardly lost during the solute transport, regardless of soil properties and structure.

For all testing soils, dye coverage was almost 100% to upper 6cm. From fully dye covered depth downward, the ratio of dye coverage decreased for all soils, ranging from 7.3% to 91%. Except for the full dye-covered depth, the dye pattern may correspond to distribution flow at upper and mid depth region, instead of preferential flow. The overall dye pattern was obviously different between undisturbed and disturbed soil D column, compared to soil C columns. The ratio of dye coverage for the undisturbed soil column D was higher than for the disturbed soil column D.

According to phenomenological transport features suggested by Flühler et al. (1996), the first 4.5cm of all soil columns can be denoted as attractor zone, where partitioning of BB to preferential flow channel is initiated. For undisturbed soil columns, this corresponds to the fact that top monolith has higher porosity and loosened soil structure, due to weather events (e.g. precipitation). Vanderborght et al. (2002) reported that densities of macropore networks

are positively correlated to lateral spreading of solute. The observed dye pattern in our study was a result of correlation between the density of macropore network and lateral spreading of solute. Preferential flow was limited to disturbed soil columns, as macropore channels were destroyed by sieving and soil mixing.

The dye patterns of all experiment column showed that non-equilibrium adsorption was dominant for BB and sulfadimethoxine. Partially, fast flow leads to non-equilibrium processes, and eventually reduced the amount of the adsorbed solutes to soil material. As shown in our batch sorption test and sorption kinetic test, BB has higher sorbility, and needs longer contact time to reach the equilibrium point than the antibiotics. Nevertheless, lateral spreading of the antibiotics could be visualized with BB to some extent, due to acceptable similarity of sorbility between BB and the antibiotics. In contrast, lateral transport of bromide did not represent lateral transport of the antibiotics, even though the ionic tracer more properly depicted water movement.

Visualization of transport pathways with BB is useful to extend understandings of sulfadimethoxine transport phenomena in soil systems. The dye pattern in horizontal cross-sections revealed that macropore and preferential flow are major flow paths for the organic compound. The distribution of the non-adsorbed tracer, bromide showed that water movement does not coincide with the transport behavior of adsorbable compounds. In contrast, sulfadimethoxine distribution can be interpreted with BB distribution, since transport behavior of BB was retarded by adsorption in soil-water interface similar to the antibiotics. The findings of the study suggest that sorption properties must be considered when selecting tracer for sorbable compounds.

Disturbance of soil destroyed macropores and preferential flow paths. This eventually leads to slow solute and water movement. Rapid water flow in macropores results in non-

equilibrium adsorption, and consequently increase the mobility of organic solutes. Therefore, soil structure should be considered for explaining and predicting fate of organic solutes as well as their physico-chemical properties.

1.5 List of manuscripts and specification of individual contributions

The three studies in the thesis refer to different manuscript. Three manuscript were submitted.

Manuscript 1

Authors	Jong Yol Park, Bernd Huwe
Title	Effect of soil structure and pH on transport of sulfonamide antibiotics
Journal	Water research
Status	submitted
Contributions	J. Park: idea, methods, experiments, analysis, modelling, manuscript writing, first and corresponding author (70%) B. Huwe: idea, manuscript editing (30%)

Manuscript 2

Authors	Jong Yol Park, Marianne Ruidisch, Bernd Huwe
Title	Transport of sulfonamide antibiotics in crop fields during monsoon season
Journal	Journal of contaminant hydrology

Status submitted

Contributions J. Park: idea, methods, experiments, analysis, modelling, manuscript writing, first and corresponding author (60%)

M. Ruidisch: idea, modelling (20%)

B. Huwe: idea, manuscript editing (20%)

Manuscript 3

Authors Jong Yol Park, Bernd Huwe

Title Sulfadimethoxine transport in soil columns in relation to sorbable and nonsorbable tracers

Journal Journal of contaminant hydrology

Status submitted

Contributions J. Park: idea, methods, experiments, analysis, modelling, manuscript writing, first and corresponding author (70%)

B. Huwe: idea, manuscript editing (30%)

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Chapter 2

Effect of soil structure and pH on transport of sulfonamide antibiotics

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ABSTRACT:

Veterinary sulfonamide antibiotics being potentially toxic to aquatic and terrestrial animals has been frequently found in environment. To describe transports of the sulfonamides in soils, their sorption characteristics and soil structures should be better understood. In this study, we investigated the effect of solution pH and soil structure on transport of sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine) relative to bromide tracer, in combination with batch sorption tests and displacement experiments. The column experiments were conducted with disturbed and undisturbed soil columns. Sulfonamides and bromide breakthrough curves were analyzed using dual-porosity model with physical non-equilibrium implemented in HYDRUS-1D. Sorption isotherms properly conformed to Freundlich model, and sorbility of the antibiotics is as follows; sulfadimethoxine > sulfamethoxazole > sulfamethazine. Decreasing pH values led to increased sorbility of the antibiotics on soil material in pH range of 4.0-8.0. This likely resulted from abundance of neutral and positive-charged sulfonamides species at low pH, which electrostatically bind to sorption sites on soil surface. The dual porosity model properly depicted the sulfonamides and bromide breakthrough curves of both the undisturbed and disturbed soil columns. Due to destruction of macropore channels, lower hydraulic conductivities of mobile zone were estimated in the disturbed soil columns than in the undisturbed soil columns, and eventually led to lower mobility of the antibiotics in disturbed column. In both of undisturbed and disturbed soil

column, transport of the antibiotics followed non-equilibrium sorption. This implies occurrence of sorption hysteresis for the sulfonamides. The results suggest that knowledge of soil structure and solution condition is required to predict fate and distribution of sulfonamide antibiotics in environmental matrix.

KEYWORDS: sulfonamide antibiotics, breakthrough curves, non-equilibrium transport, reactive transport, process modelling

2.1 Introduction

The presence of trace levels of antibiotics in the environmental system has concerned to developed regions as well as international organizations. These bioactive compounds have been found in various types of environmental matrices, such as soil, surface and ground water. Even though several studies have shown occurrence of antibiotics in environment, their fate and transport are not well understood. They can enter to the environment after excreted by animals and accidentally released during manufacturing and discarding. In general, veterinary medicines cannot be fully metabolized by physiological pathways in animals. For several veterinary medicines, up to 90% of the applied amounts directly excreted through urine and faces as parent compounds (Kümmerer and Henninger, 2003). Metabolites of the medical compounds can still have bioactivity, and may bring negative effects on aquatic and terrestrial ecosystems. The collected manure from husbandry is used as organic fertilizer, and is a major source of antibiotics in agricultural regions.

As an important group of veterinary pharmaceuticals, sulfonamide antibiotics have intensively been studied with respect to their occurrence and fate in environmental matrices. The majority of studies have attested the general presence of sulfonamides in soils from ng/L up to μg/L level and at relatively low levels in water. For example, sulfadimethoxine was detected up to mg/kg level (Boxall et al., 2004). Sulfamethoxazole is as high as 1.9 μg/L in

river water (Hirsch et al., 1999; Kolpin et al., 2002).

Understanding the fate and transport of sulfonamide drugs in environment plays a key role in accurate assessment of their behaviour. Adsorption can be a limiting factor of subsurface transport and biodegradation by microorganisms in soil (Boxall et al., 2004; Thiele-Bruhn et al., 2004). The adsorption coefficients of sulfonamides vary with soil composition, texture, and natural organic matter. (Thiele-Bruhn et al., 2004; Gao and Perdersen, 2005). For acidic organic compounds, pH-dependent sorption to soil materials can effect on their mobility and distribution in soil-water interfaces (Tülp et al., 2009; Bronner et al., 2010).

The objective of this study is to improve the understanding of sorption and transport of sulfonamide antibiotics in soils, using batch adsorption tests and column displacement experiments under different pH levels. Transport of the antibiotics was evaluated in disturbed and undisturbed soil columns in order to describe effect of soil structure on their movement and fate in different soil system. The process-based physical and chemical transport model, HYDURS-1D was used to estimate hydraulic and solute transport parameters by inverse modelling.

2.2 Materials and methods

2.2.1 Soil sampling area and soil description

Soil columns were taken in Haean catchment located at north-east of Gangwon province, South Korea (N 38° 16', E 128° 8' and N 38° 14', E 128° 7'). The area represents one of the largest highland-farming regions in Soyang watershed. The catchment has the variability in complex landuse, which can be mainly categorized in the rice paddy zone, the dryland farming area and the forest vegetation belt. Approximately 27% of the Haean catchment was occupied

by agricultural field (rice paddy + dry farmland).

As a source of plant nutrients, a huge amount of manure generated from swain, cattle and poultry is applied to the crop fields. In this region, environmental issues of animal manure application were principally associated with nutrients leaching and transport during monsoon season. However, other constituents are recently issued, such as veterinary pharmaceuticals and pathogens. Although presence of the veterinary medicines in the animal manure has been addressed in recent reports (KFDA, 2006), the loadings to the crop fields and their transport behaviour in the catchment are only beginning to be identified.

Soil properties shows in Table 2.1. The soil columns are typical sandy-loam, due to adding sandy soil to the top soil layer of the crop fields to compensate for soil loss. After corns were manually harvested, no agricultural activities were performed in the lands for about 1 years in order to recover soil nutrients. We analysed residual concentration of the target sulfonamides (sulfamethoxazole, sulfadimethoxine and sulfamethazine) in the soil columns before applying the veterinary antibiotics. No pharmaceuticals were detected at the soils.

Table 2.1 Physical and chemical soil properties of two fields

	Soil A	Soil B
Texture (%)[a]		
	Sand: 74.5	Sand: 65.2
	Silt: 20.0	Silt:26.7
	Clay: 5.5	Clay: 8.1
Bulk density(g/cm^3)	1.42	1.34
Organic carbon (%)	2.21	2.97
pH	5.7	5.5

[a] According to soil texture classification system from USDA(United States Department of Agriculture).

2.2.2 Chemicals and reagents

Sulfamethoxazole, sulfadimethoxine and sulfamethazine were purchased from Sigma-Aldrich (Seelze, Germany). Isotope-labeled compounds (sulfamethoxazole-D_4, Sulfadimethoxine-D_4 and Sulfamethazine-D_4) were obtained from Toronto Research Chemicals Inc. (North York, Ontario, Canada). Methanol, acetonitrile and water for HPLC-MS-MS analysis were purchased from Sigma-Aldrich and Th. Geyer GmbH (Renningen, Germany).

2.2.3 Analysis of antibiotics

The target sulfonamides in leachate were analysed using high-performance liquid chromatography with tandem mass spectrometry (Quattro micro TM API, Waters, Milford, MA). Sulfamethoxazole-D_4, sulfadimethoxine-D_4 and sulfamethazine-D_4 were used as internal standard. Before analysis, the aqueous sample was filtered through a 0.22μm PES membrane (Millipore, Billerica, MA) to separate suspended particles in sample. Operation condition of HPLC was described as table 2.2 and 2.3 in detail.

Table 2.2 HPLC gradient program and flow rate

Time(min)	Eluent A(%)	Eluent B(%)	Flow rate(ml/min)
0.00	90	10	0.2
2.00	90	10	0.2
10.00	10	90	0.2
15.00	10	90	0.2
16.00	90	10	0.2
25.00	90	10	0.2

Eluent A: Water with 0.1% formic acid, Eluent B: Acetonitrile with 0.1% formic acid

Table 2.3 Information of HPLC-MS-MS operation condition to determine 3 sulfonamides

Compound	Retension Time(min)	Parent mass	Daughter mass	Cone Volt.	Collision Energy
Sulfamethoxazole	13.567	254	156	25	16
Sulfamethoxazole-d_4	13.576	258	160	25	16
Sulfamethazine	13.060	279	186	30	18
Sulfamethazine-d_4	13.043	283	186	30	20
Sulfadimethoxine	14.031	311	156	30	22
Sulfadimethoxine-d_4	14.012	315	156	30	23

Internal standard: Sulfamethoxazole-d_4, Sulfamethazine-d_4, Sulfadimethoxine-d_4

2.2.4 Batch sorption experiments

The soils taken from the field sites were transported to the laboratory, and were dried in 60℃. Properties of the soils was measured, such as soil texture, carbon contents and pH. Soil texture measurement was performed by laser diffraction analyser (Mastersizer S MAM5004, Malvern Instrument GmbH, Herrenberg, Germany), respectively.

Target chemical solutions were prepared using sulfamethoxazole, sulfadimethoxine and sulfamethazine dissolved in methanol. Sorption studies were conducted in 30ml glass tubes operated as completely mixed batch system. Three replicate tubes were prepared for each treatment by adding 2g of dry soil and 10ml of working solution (pH 4.0-8.0) containing 0.01M KBr to pre-weighed tubes. Treatments include three initial aqueous concentrations, five different concentrations. Losses caused by sorption are quantified with control tubes that contained no soil materials. The contents of the tubes were homogenized with a shaker at room temperature for 24 hours. At the end of the contact time, the tubes were centrifuged for 20min at 1500rpm and then the aliquots were filtered with 0.22μm PES membrane (Millipore,

Billerica, MA). The antibiotics remaining in the aqueous aliquot is measured by HPLC-MS-MS.

The experimental data of the equilibrium adsorption isotherm for the sulfonamides were represented by Freundlich isotherm model considering multilayer adsorption over heterogeneous surface. Freundlich isotherm is given as:

$$q_e = K_f C_e^{1/n}$$

where q_e is amount of adsorbate in the adsorbent at equilibrium (mg/g), and C_e represents equilibrium concentration (mg/L). K_f is Freundlich isotherm constant (mg/g), and 1/n is adsorption intensity related to adsorption capacity.

2.2.5 Column transport experiment

Undisturbed soil columns were taken from the mentioned field sites using same stainless cylinder with 15cm inner diameter and 30cm length. Disturbed soil columns were packed with the same soils sieved with 2mm mesh, using cylinders of the same dimensions. 0.02 M calcium chloride was applied for 24 hr onto top of the soil columns at a rate of 5.6 ml/min to maintain steady-rate flow. After the wetting, aqueous solutions with each sulfonamide antibiotic (1mg/L) and KBr (1g/L) were applied to disturbed and undisturbed soil columns. Application of aqueous solution into soil columns was controlled by a peristaltic pump with 5.6 ml/min. Leachate from the bottom of each soil column was automatically collected every 5 minutes in 30ml glass vial. Residual concentrations of the sulfonamides and conservative tracer, bromide in the aqueous sample were determined with HPLC-MS-MS and an ion-selective electrode (Metrohm, Zofingen, Switzerland) in combination with a reference electrode.

2.2.6 Numerical Modelling and Process Identification

In order to simulate water flow and solute transport in various porous media, several numerical modelling software have been developed in the past. Most of modelling tools are coupling water flow and solute transport. HYDRUS-1D considers coupling of water flux and solute transport in liquid phase according to Richards equation and advective-dispersive equation. Adsorption-desorption (e.g. Langmir and Freundlich isotherm equation) and degradation (e.g. kinetic degradation) of reactive solute are adapted to the modelling tool. Applicability of the modelling tool was well proved in previous studies under application of various organic solutes and soil system (Casey and Šimůnek, 2001; Suárez et al., 2007). In this research, numerical modelling was performed with HYDRUS-1D (Version 4.15, PC-Progress s.r.o.), since a key strength of the modelling is use of Richards equation to estimate water flow in unsaturated soils.

To describe unsaturated water flow, HYDRUS-1D solves Richards equation by finite element method. Solute transport is simulated by advection-dispersion equation based on the modified Fick's law. For non-reactive tracer, it can be given for steady rate conditions and homogeneous soils as follows (Šimůnek et al., 2012):

$$\frac{\partial C}{\partial t} = -\nu \frac{\partial C}{\partial z} + D \frac{\partial^2 C}{\partial z^2} \qquad (1)$$

Where t is time [T], ν is pore-water velocity [LT^{-1}], C is solute concentration in aqueous phase [ML^{-3}], D is dispersion coefficient [L^2T^{-1}] and z is depth [L]. Bromide breakthrough curve was used to calculate ν and D by parameter estimation method based on inverse model applied to Hydrus-1D (version 4.14).

In order to depict transport of applied sulfonamide antibiotics in soil column, physical nonequilibrium solute transport model was used. The solute transport model is account for by

assuming a two region, mobile (θ_{mo}) and immobile (θ_{im}) region (van Genuchten and Wierenga, 1976).

$$\theta = \theta_{mo} + \theta_{im} \tag{2}$$

In the model, it is assume that water and solute exchange occurs between two regions, and the process is generally calculated by first-order equation. The dual-porosity model for water flow consists of the Richards equation to depict water flow in the mobile region and a mass balance equation to describe water movement in matrix as bellows:

$$\frac{\partial \theta_{mo}}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z} + 1\right)\right] - S_{mo} - \Gamma_w \tag{3}$$

$$\frac{\partial \theta_{im}}{\partial t} = -S_{im} + \Gamma_w \tag{4}$$

Where S_{mo} and S_{im} are sink terms for both regions, and Γ_w is the mass transfer rate for water from immobile region and mobile region.

The water flow and reactive solute transport is coupled by the following equation, based on convection-dispersion equation and mass balance equation as follows (Šimůnek et al., 2012):

$$\frac{\partial \theta_{mo} c_{mo}}{\partial t} + f_{mo}\rho \frac{\partial S_{mo}}{\partial t} = \frac{\partial}{\partial z}\left(\theta_{mo} D_{mo} \frac{\partial c_{mo}}{\partial z}\right) - \frac{\partial q_{mo} c_{mo}}{\partial z} - \emptyset_{mo} - \Gamma_s \tag{5}$$

$$\frac{\partial \theta_{im} c_{im}}{\partial t} + (1 - f_{mo})\rho \frac{\partial S_{im}}{\partial t} = \Gamma_s - \emptyset_{im} \tag{6}$$

$$\Gamma_s = \omega(c_{mo} - c_{im}) + \Gamma_w c \tag{7}$$

In the above equation, C_{mo} and C_{im} are concentrations of the mobile and immobile

regions [ML^{-3}]; S_{mo} and S_{im} are sorbed concentrations of the mobile and immobile regions [-]; D_{mo} is the dispersion coefficient in the mobile region [L^2T^{-1}], q_{mo} is the volumetric fluid flux density in the mobile region [LT^{-1}], f_{mo} and f_{im} are sink/source terms that accounts for various zero- and first-order or other reactions in both regions [$ML^{-3}T^{-1}$]; f_{mo} is the fraction of sorption sites in contact with the mobile water content [-]. Γ_w is rate of mass transfer between the mobile and immobile region. The equation (5) is solute transport in the mobile zone, and the equation (6) depicts a mass balance for the immobile zone. The equation (7) describes the rate of mass transfer between the mobile and immobile zone.

HYDRUS-1D has parameter optimization module for estimating water flow and solute transport parameters from steady-state and transient water flow system. In this study, hydraulic and solute model parameters were optimized using inverse modelling, which implements in HYDRUS-1D. The inverse modelling based on the minimization of an objective function defined by Šimůnek et al., expressing the discrepancy between the simulated system response and observed values (Šimůnek et al., 2012). Minimization of the objective function is performed by using Levenberg-Marquardt nonlinear minimization method. Coefficients of determination (R^2) for the observed versus the simulated values of the sulfonamides concentrations and bromide in leachate were estimated for quality assurance of the modelling.

2.3 Results and discussions

2.3.1 Batch Sorption Experiments

Two soils collected from agricultural land were used for the adsorption experiment. Effect of pH on adsorption characteristics was investigated, and sorption parameters based on Freundlich isotherm were estimated by nonlinear regression method. Adsorption coefficient

(K_d) and Freundlich adsorption coefficient (K_f) of selected antibiotics are listed in Table 2.4 and Table 2.5. Sorption of sulfamethazine, sulfamethoxazole and sulfadimethoxine was properly regressed for both soils taken agricultural region. In range of pH 4.0 and 8.0, the adsorption coefficient (K_d) was strongly dependent on pH. It means that all chosen sulfonamide antibiotics were easily adsorbed onto soil materials in low pH of aqueous solution. Sulfadimethoxine had higher adsorption coefficient (K_d) value than other sulfonamides under weak acid and neutral condition (pH 4.0-7.0). As given Table 2.4 and 2.5, adsorption of sulfadimethoxine strongly was affected by change of pH value in test solution, compared to sulfamethoxazole and sulfadimethoxine.

Table 2.4 Adsorption parameter of sulfonamide antibiotics based on Freundlich isotherm for soil A (standard error)

Antibiotics	pH	K_d (L kg^{-1})	K_f (L kg^{-1})	1/n	R^2
Sulfamethazine					
	4.0	1.32 (0.04)	1.53 (0.03)	0.76 (0.02)	0.99
	4.5	1.19 (0.04)	1.46 (0.02)	0.70 (0.01)	0.99
	5.0	1.23 (0.04)	1.48 (0.02)	0.72 (0.02)	0.99
	5.5	1.05 (0.03)	1.28 (0.03)	0.73 (0.03)	0.99
	6.0	0.95 (0.03)	1.19 (0.02)	0.71 (0.02)	0.99
	7.0	0.87 (0.02)	1.05 (0.02)	0.79 (0.02)	0.99
	8.0	0.80 (0.02)	0.92 (0.03)	0.84 (0.03)	0.99
Sulfamethoxazole					
	4.0	1.48 (0.05)	1.77 (0.01)	0.69 (0.01)	0.99
	4.5	1.49 (0.03)	1.66 (0.02)	0.80 (0.02)	0.99
	5.0	1.44 (0.03)	1.61 (0.02)	0.80 (0.02)	0.99
	5.5	1.39 (0.02)	1.51 (0.02)	0.86 (0.02)	0.99
	6.0	1.27 (0.01)	1.31 (0.02)	0.95 (0.02)	0.99
	7.0	1.05 (0.02)	1.13 (0.02)	0.89 (0.02)	0.99
	8.0	1.03 (0.02)	0.91 (0.03)	0.91 (0.03)	0.99
Sulfadimethoxine					
	4.0	2.33 (0.03)	2.39 (0.02)	0.89 (0.02)	0.99
	4.5	2.22 (0.05)	2.35 (0.02)	0.80 (0.01)	0.99
	5.0	1.83 (0.04)	1.98 (0.02)	0.81 (0.02)	0.99
	5.5	1.63 (0.02)	1.65 (0.03)	0.98 (0.03)	0.99
	6.0	1.45 (0.02)	1.52 (0.03)	0.91 (0.03)	0.99
	7.0	1.23 (0.02)	1.22 (0.03)	1.01 (0.03)	0.99
	8.0	1.01 (0.02)	1.07 (0.03)	0.92 (0.04)	0.99

Table 2.5 Adsorption parameter of sulfonamide antibiotics based on Freundlich isotherm for soil B (standard error)

Antibiotics	pH	K_d ($L\ kg^{-1}$)	K_f ($L\ kg^{-1}$)	1/n	R^2
Sulfamethazine					
	4.0	1.15 (0.04)	1.38 (0.02)	0.74 (0.02)	0.99
	4.5	1.05 (0.03)	1.22 (0.03)	0.79 (0.02)	0.99
	5.0	1.04 (0.03)	1.19 (0.03)	0.82 (0.03)	0.99
	5.5	0.98 (0.02)	1.14 (0.01)	0.81 (0.01)	0.99
	6.0	1.02 (0.01)	1.11 (0.01)	0.89 (0.02)	0.99
	7.0	0.92 (0.01)	1.01 (0.01)	0.88 (0.01)	0.99
	8.0	0.90 (0.01)	0.93 (0.02)	0.96 (0.03)	0.99
Sulfamethoxazole					
	4.0	1.34 (0.04)	1.57 (0.02)	0.74 (0.01)	0.99
	4.5	1.24 (0.03)	1.40 (0.02)	0.81 (0.02)	0.99
	5.0	1.14 (0.02)	1.29 (0.02)	0.82 (0.02)	0.99
	5.5	1.10 (0.01)	1.18 (0.02)	0.90 (0.02)	0.99
	6.0	1.11 (0.02)	1.16 (0.02)	0.93 (0.02)	0.99
	7.0	0.95 (0.01)	1.01 (0.02)	0.92 (0.02)	0.99
	8.0	0.93 (0.02)	0.94 (0.03)	0.98 (0.03)	0.99
Sulfadimethoxine					
	4.0	1.92 (0.05)	2.11 (0.02)	0.77 (0.01)	0.99
	4.5	1.78 (0.04)	1.92 (0.03)	0.83 (0.02)	0.99
	5.0	1.52 (0.03)	1.66 (0.03)	0.83 (0.02)	0.99
	5.5	1.36 (0.02)	1.49 (0.01)	0.85 (0.01)	0.99
	6.0	1.29 (0.02)	1.36 (0.02)	0.91 (0.02)	0.99
	7.0	1.01 (0.01)	1.09 (0.01)	0.89 (0.01)	0.99
	8.0	0.86 (0.01)	0.87 (0.02)	0.99 (0.03)	0.99

The pH-dependent sorption of chosen antibiotics results from their acid-base properties in aqueous solution. The sorption reaction was consistent with the changes in the fraction of ionized sulfonamide antibiotics, since they transform from their cationic species to neutral and anionic species with increasing pH. Positive- and neutral- charged forms are electrostatically bound to negative-charged surface of soil mineral. Presence of soil organic matters can also cause the pH-dependent sorption. A large portion of soil organic matter is in neutral form at low pH, and the hydrophobic neutral species also sorbs to the soil functional groups more than the anionic species instead of the sulfonamides (Fontaine et al. 1991). Consequently, higher K_d and K_f values were estimated at low pH in this study.

Freundlich-type isotherm depicted more properly than Langmuir and linear isotherm. This was based on the R^2 values obtained from the different isotherms, as given in Table 2.4 and 2.5. The 1/n value of Freundlich isotherm for the antibiotics are in the range 0.69-1.01. A $1/n < 1$ indicates that the marginal sorption energy of the sorbates decreases with increasing surface concentration (Brusseau et al., 1989; Weber et al., 1991). For the sulfonamides, the Freundlich-type isotherm was attributed to varying sorption energy and adsorption which is presumably based on site-specific mechanisms. This was frequently reported for the both hydrophobic and hydrophilic sorbates (McGinley et al., 1996; Gunasekara and Xing, 2003; Huang et al., 1997).

2.3.2 Bromide transport in undisturbed and disturbed soil columns

Column experiments were conducted in order to compare transport and fate of bromide and chosen sulfonamide antibiotics in soils with different structure and pore condition. Breakthrough curves were plotted with relative concentration of bromide in leachate against the number of pore volumes applied in soil columns, defined as V/V_0, where V is the applied

volume of solute and V_0 is the pore volume of the soil column. As shown Fig. 2.1, breakthrough curve for undisturbed soil columns had earlier arrival times and peak times than those observed in disturbed soil column. The number of pore volumes when bromide concentration in leachate at elution phase was higher for undisturbed soil columns (Soil A: 0.54-0.57, Soil B: 0.52-0.58) than for disturbed columns (Soil A: 0.64-0.67, Soil B: 0.71-0.75). This offers occurrence of preferential flow in all undisturbed soil columns. The bromide breakthrough curves were fitted to similar shape in both the undisturbed and disturbed soil column. Breakthrough curve and hydraulic parameter estimation with Hydrus-1D reveals that bromide transport, i.e. a conservative tracer was a typical convection-dispersion process without sorption and degradation. Tailing of bromide breakthrough curve indicated that the conservative tracer transport was a physical nonequilibrium process. In particular, tailing of bromide breakthrough curve was properly depicted by dual porosity model with physical nonequilibrium process.

Table 2.6 Hydraulic parameters of soil columns

Soil column	θr (m^3/ m^3)	θs (m^3/ m^3)	K_s (m/hr)	α (m^{-1})	n (-)	D (m)
Soil A (undisturbed)	0.051	0.366	0.0232	3.18	1.58	0.038
Soil A (disturbed)	0.064	0.387	0.0176	2.94	1.74	0.035
Soil B (undisturbed)	0.061	0.383	0.0287	3.31	1.61	0.045
Soil B (disturbed)	0.066	0.412	0.0203	3.14	1.76	0.030

In the present study, transport of the conservative tracer was dependent only on the water movement in soil system. Fig. 2.1 shows that the water flow and bromide transport in disturbed soil was relatively retarded than in undisturbed soil column. Delay of the peak time and earlier arrive time can be explained by difference of physical properties (e.g. hydraulic and

solute parameter) between disturbed and undisturbed soil column. As the soil materials sieved with 2mm mesh were used to pack in soil column, the large soil particles and aggregates were excluded in disturbed soil column. In particular, burrows developed by earthworm, plant roots and cracks were found in the undisturbed columns. Consequently, the preferential flow was active in the macropores. The soil disturbance led to eliminate macropore channel in disturbed soil columns, and therefore matrix flow was dominant in disturbed soil columns. The elimination of the coarse particles and macropore channel caused relatively low hydraulic conductivity in disturbed soil column.

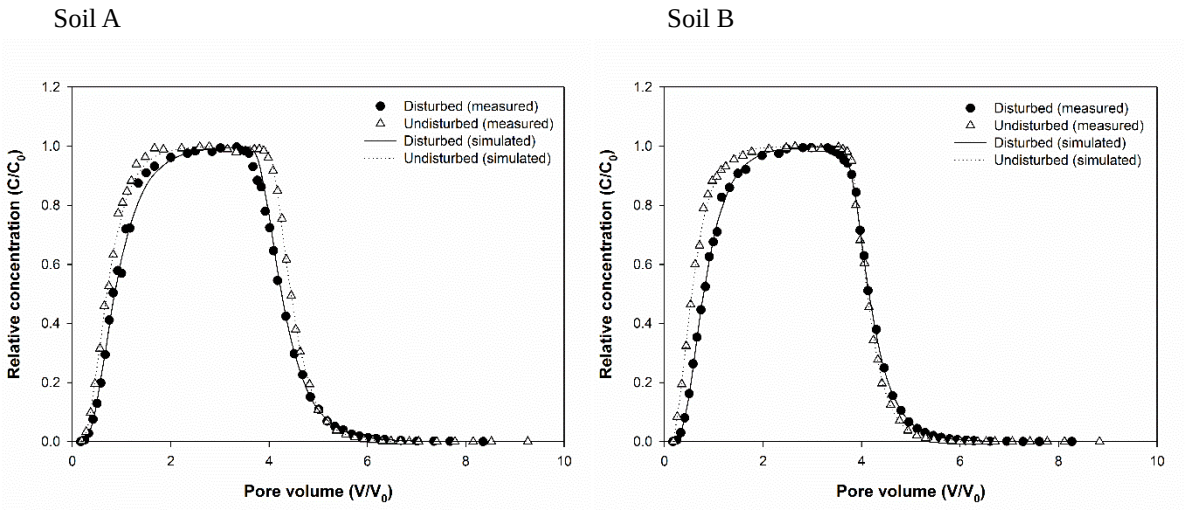


Fig. 2.1 Bromide breakthrough curves for undisturbed and disturbed soil columns. (pH 4.0)

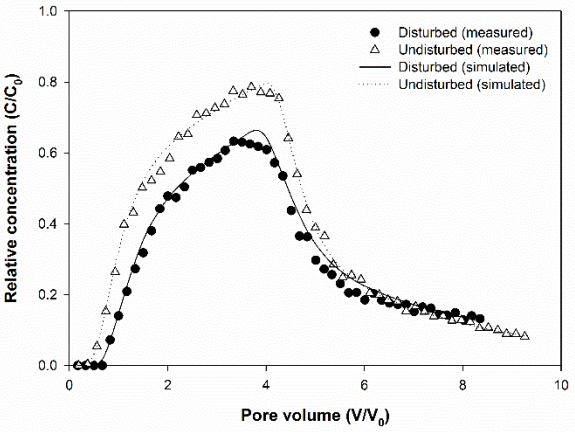
Longitudinal dispersivity values were estimated for undisturbed (Soil A: 3.6-4.0cm, Soil B: 4.1-4.5cm) and disturbed soil columns (Soil A: 3.1-3.4 cm, Soil B: 2.9-3.5cm). The dispersivity at column scale is dependent on the homogeneity of soil structure and pore-size distribution. Low longitudinal dispersivity reflects homogenous pore system or short flow-channel length (Shaw et al., 2000). Relatively higher longitudinal dispersivity values were obtained for undisturbed soil columns. Pore distribution of the disturbed columns was more homogeneous, since relatively fine soil particles (<2mm) were packed. Consequently, higher

hydraulic conductivity and longitudinal dispersivity reflects heterogeneous soil structure for the undisturbed soil columns.

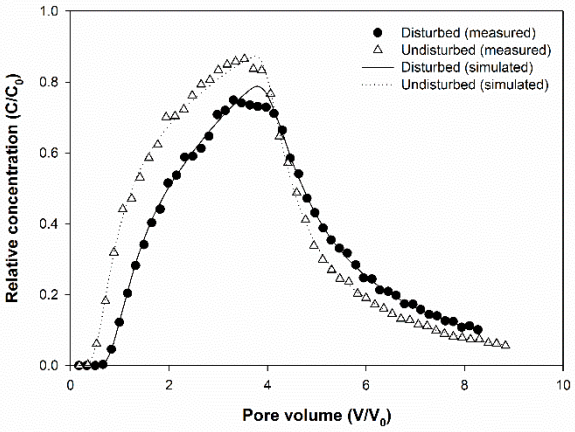
2.3.3 Transport of sulfonamide antibiotics in undisturbed and disturbed soil column

Sulfonamides breakthrough curves obtained from undisturbed soil columns had earlier peak time than those observed in disturbed soil columns, as bromide breakthrough curves. Breakthrough curves of the chosen sulfonamides showed tailing pattern in desorption phase. The long tail of sulfonamides breakthrough curves in the column effluent proved that the transport process was nonequilibrium and hysteresis-based transport. The sorption hysteresis of the sulfonamides was reported, and this is relevant to slower desorption through covalent bonding to organic matters (Bialk and Peterson 2008; Sukul et al., 2008). Different shape and peak time among the sulfonamides breakthrough curves was found in both undisturbed and disturbed soil column. The peak time of the sulfonamides was strongly dependent on the Freundlich adsorption coefficient (K_f) estimated by inverse model in Hydrus-1D. Sulfadimethoxine breakthrough curves had relatively high value of peak time and long tailing than sulfamethoxazole and sulfamethazine breakthrough curve. The delay of peak time apparently reflects that the adsorption were one of the central governing processes to depict the transport of sulfonamides in soil.

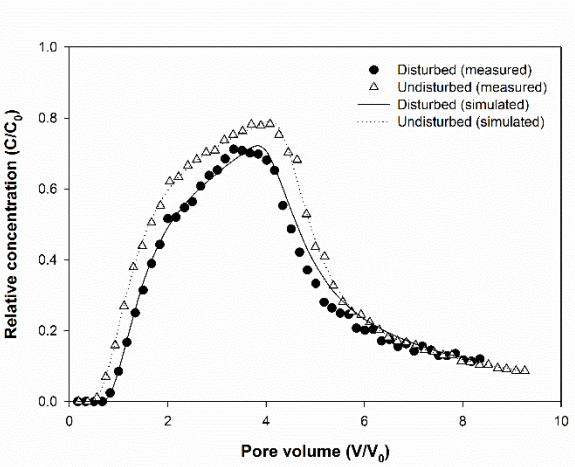
Sulfamethoxazole – Soil A



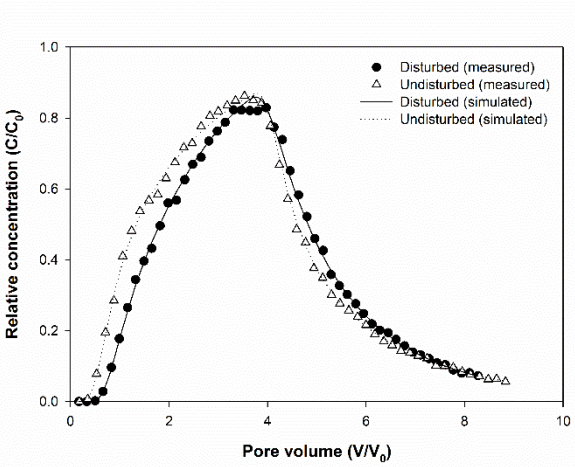
Sulfamethoxazole – Soil B



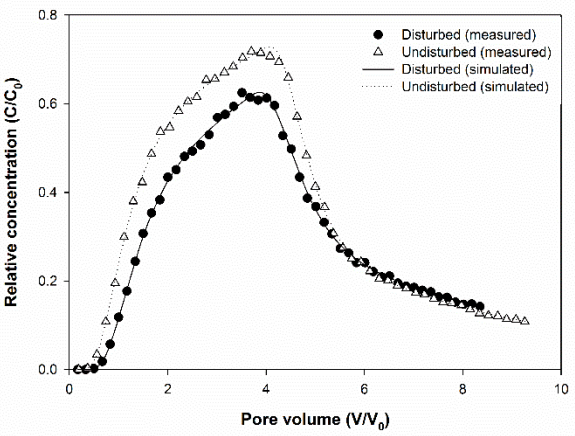
Sulfamethazine – Soil A



Sulfamethazine – Soil B



Sulfadimethoxine – Soil A



Sulfadimethoxine – Soil B

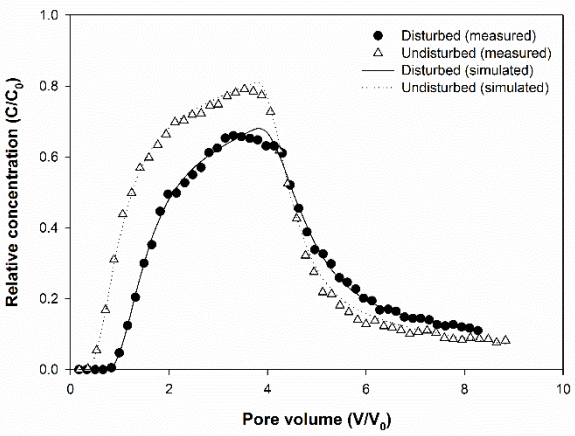


Fig. 2.2 Sulfonamide breakthrough curves for undisturbed and disturbed soil columns. (pH 4.0)

Recovery rate of the sulfonamides was higher in the undisturbed column (sulfamethoxazole: 75.6-83.7%, sulfadimethoxine: 66.4-78.7%, sulfamethazine: 75.5-83.9%) than disturbed column (sulfamethoxazole: 64.3-81.6%, sulfadimethoxine: 65.4-81.8%, sulfamethazine: 67.6-85.1%). The recovery of sulfadimethoxine is relatively low, comparing to the other chosen sulfonamides. The recovery rate can presumably result from the degradation by microorganisms and irreversible sorption between the applied solutes and surface of soil particles. As degradation of the sulfonamide antibiotics in the column was ignorable for the experiment, the irreversible sorption in soil columns could induce the different recovery rate. The irreversible sorption of organic solutes-geosorbent systems has been revealed in previous studies (Boivin et al., 2005; Kan et al., 1994; Weber et al., 1998).

The dual-porosity model can consider equilibrium and nonequilibrium transport of solutes to analyze the breakthrough curves. Solute parameter optimization of the breakthrough curves were conducted with Freundlich isotherm parameters (i.e. K_f and n) obtained from batch sorption experiments. The dual-porosity model with the batch adsorption parameters cannot simulate sulfonamides breakthrough curves properly, regardless of soil structure and pH value in applied aqueous solution, since sorption behavior was overestimated in the simulation. Sorption parameter estimation with inverse model shows that lower K_f values were estimated for both undisturbed and disturbed soil columns than for the batch sorption experiment. K_f values for disturbed soil columns was higher, comparing to undisturbed soil columns. The difference was caused by relatively longer retention time which assures to shift to equilibrium state for sorption reaction. The parameter estimation provided that K_f values for disturbed soil columns were relatively lower. Overall, this result indicates that the sulfonamide antibiotics movement was nonequilibrium. Sorption behaviour in soil columns were presumably affected by rate-limited mass transfer between adsorption site and the applied solutes, due to fast solute advection.

Several studies have shown that sophisticated water movement in natural soil can be properly described with dual-porosity models (Gerke and Genuchten, 1993; Everts and Kanwar, 1990). Climate events (e.g. precipitation) and subterranean animal activities generate macropore and fracture where water flow is relatively faster than matrix flow, indicating preferential flow. In the most situations, soils taken from agricultural regions consist of various mineral particles, rock fragment and organic materials. The heterogeneity of soil composition also induced different types of flow path. Therefore, dual-porosity model also can depict water movement in disturbed soil system.

In Hydrus-1D, solute transport was coupled with water flow based on Richards equation, and advection-dispersion, sorption and degradation are considered in the Hydrus-1D. Freundlich isotherm is implemented to allow for nonequilibrium considerations of adsorption reaction (Šimůnek et al., 2012). Two-region sorption assumes that solute partitioned into two phases (mobile and immobile zone) and adsorption-desorption reaction occurs in each region. Exchange between two regions is considered by using exchange term which reflects mainly diffusive mass transfer under complex geometrical conditions. The coupling among solute reaction and water flow in both mobile and immobile zone enables the simulation of water movement and solute reaction simultaneously in complex system (Šimůnek et al., 2012).

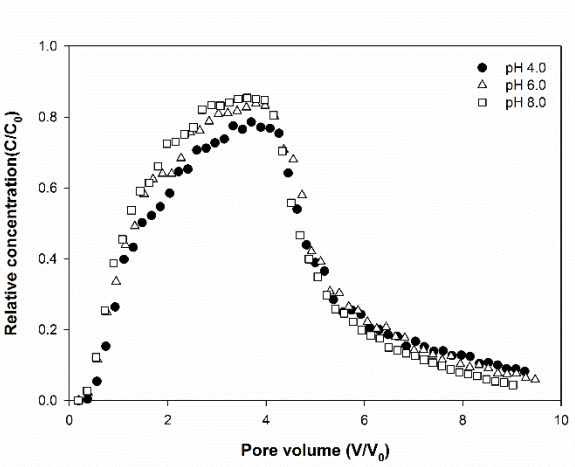
Degradation and transformation of the sulfonamide antibiotics was negligible in column experiment. Result of inverse parameter estimation offered that degradation of the antibiotics was small in soil column. The estimate was reliable because several studies reported that degradation of sulfonamide antibiotics in soil and soil-water interface is a slow reaction (Wang et al., 2006; Yang et al., 2009).

2.3.4 pH-dependent transport of sulfonamide antibiotics

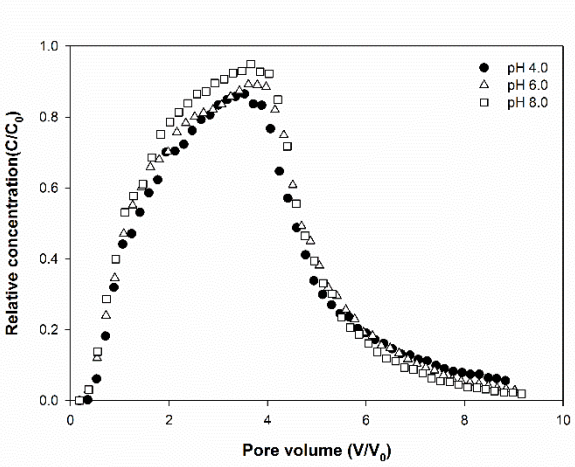
Column experiments for sulfonamide antibiotics was performed at different pH values. The pH of solute was measured before and after leaching process, and the difference between two measured pH values was less 0.3 for all samples. Comparison of sulfonamide breakthrough curves for pH change shows in Fig. 2.3. Consequently, it is obviously that transport of the chosen sulfonamides was typically pH-dependent, for difference of sulfonamides breakthrough curves among different pH.

As increasing pH value in applied solution, peak concentrations of the sulfonamides in leachate were increased, regardless of the soil origin and homogeneity. It pronounces that the sulfonamides were transported quickly through the soil columns in high pH condition. First detection time of the sulfonamides was delayed as decreasing pH. In particular, the detection time significantly changed in disturbed soil column than in undisturbed column. Relatively higher retention time in disturbed soil columns assures that the antibiotics more approach to sorption equilibrium. Under this condition, effect of pH was clearly revealed, comparing to undisturbed soil columns where faster water flow was observed. All sulfonamide breakthrough curves were typically asymmetric, and had tailing for desorption phase, indicating that nonequilibrium adsorption occurred in soil-water interface. As given Fig. 2.3, transport of sulfadimethoxine in soil column was most sensitive to pH among the chosen antibiotics. For sulfadimethoxine, difference of peak value was more than 0.13, and tailing in desorption phase was more shortened, as increasing pH values. This is consistent with the highest increment of K_d for sulfadimethoxine among the sulfonamide antibiotics in the column experiments (Table 2.7 and 2.8).

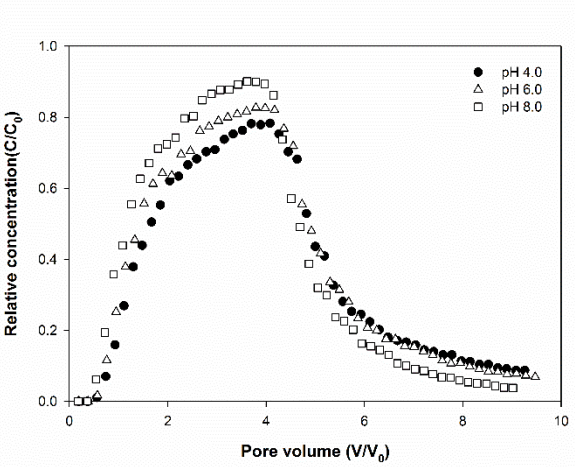
Sulfamethoxazole- undisturbed Soil A



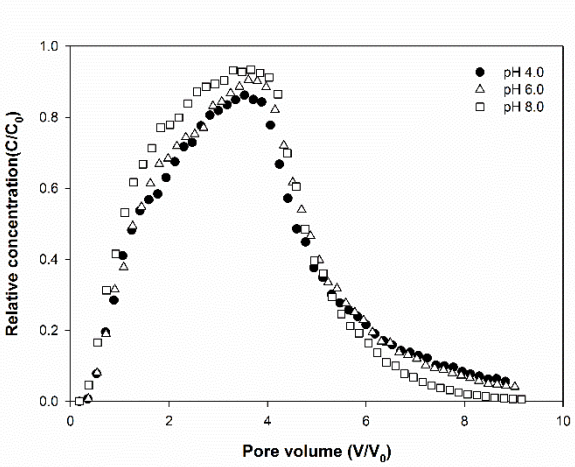
Sulfamethoxazole- undisturbed Soil B



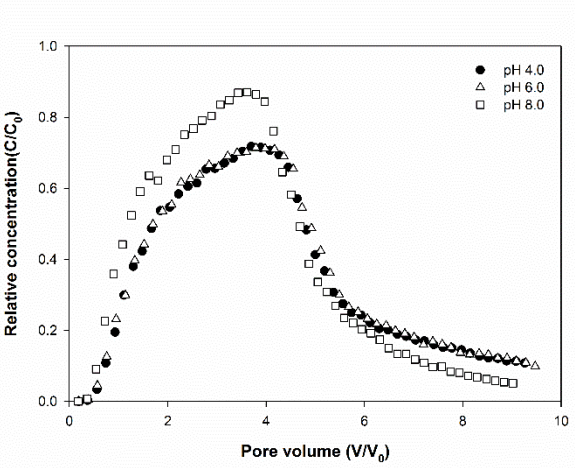
Sulfamethazine- undisturbed Soil A



Sulfamethazine- undisturbed Soil B



Sulfadimethoxine- undisturbed Soil A



Sulfadimethoxine- undisturbed Soil B

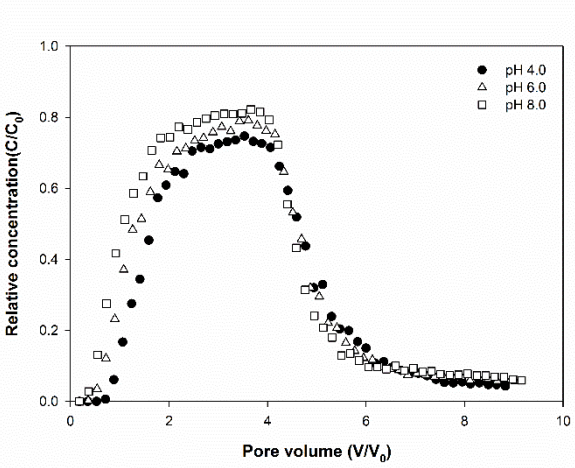


Fig. 2.3 Sulfonamide breakthrough curves at different pH

Table 2.7 Solute parameters of soil columns – undisturbed soil A

Sulfonamide	pH	K_f (L/kg)	n (-)	μ (d^{-1})
Sulfamethoxazole	4.0	0.53	0.84	0.0003
	6.0	0.41	0.93	0.0003
	8.0	0.35	1.03	0.0003
Sulfamethazine	4.0	0.60	0.84	0.0003
	6.0	0.46	0.72	0.0004
	8.0	0.29	0.73	0.0003
Sulfadimethoxine	4.0	0.79	0.96	0.0003
	6.0	0.52	0.83	0.0003
	8.0	0.35	0.78	0.0004

In the present study, it is hypothesized that effect of pH on their mobility and adsorption is dependent on substitution group (-R). For soil columns, the effects of sulfonamide substituent were evaluated by comparison of their nonequilibrium sorption coefficient estimated from their breakthrough curves. The effects of pH on sulfonamide transport were relevant to their pK_a and isoelectronic points (sulfadimethoxine: 4.0, sulfamethoxazole: 3.9, sulfamethazine: 4.9). Distribution among sulfamethazine species was relatively more influenced by solution pH in the range of pH 4.0 to 8.0, since the interval between pK_{a1} (2.4) and pK_{a2} (7.4) is smaller than other two sulfonamides. Below isoelectronic point, positive and neutral forms of sulfonamide are dominant in aqueous solution. Since surface of soil mineral is generally negatively charged, electrostatical interaction can be easily induced between soil and the non-negative form. At same pH, partitioning of the each sulfonamide antibiotic is therefore determined by abundance of non- negative species associated with type of the substitution group. This is consistence with the findings of our batch sorption experiments and previous studies (Avisar et al., 2010).

Table 2.8 Solute parameters of soil columns – undisturbed soil B

Sulfonamide	pH	K_f (L/kg)	n (-)	μ (d^{-1})
Sulfamethoxazole	4.0	0.50	0.75	0.0003
	6.0	0.36	1.01	0.0004
	8.0	0.30	0.91	0.0003
Sulfamethazine	4.0	0.52	0.84	0.0003
	6.0	0.40	0.83	0.0003
	8.0	0.28	1.09	0.0004
Sulfadimethoxine	4.0	0.70	0.83	0.0002
	6.0	0.44	0.79	0.0003
	8.0	0.35	0.97	0.0002

The shortness of early detection time and peak time for the sulfonamides as pH increased were in good agreement with change of K_d values obtained from column experiment, not from batch condition, due to nonequilibrium sorption between soil-solute interface. Besides, according to parameter estimation by inverse model and previous studies, degradation rate of the sulfonamides was ignorable in soil columns for whole testing pH (Accinelli et al., 2007).

2.4 Conclusion

In this study, the influence of pH on transport and fate of three sulfonamide antibiotics was investigated in combination with the batch sorption tests and the soil column experiments. The batch sorption experiments showed Freundlich sorption isotherm can describe their adsorption behaviours under different pH, respectively. The batch experiments also revealed that increasing sorbility was observed with decreasing pH for the all sulfonamides, since

neutral and positive species being able to electrostatically bind to surface of soil mineral were abundant under acidic conditions. The dependency is one of important factors for interpretation of transport and fate of the veterinary antibiotics in soil-water system. Among the testing sulfonamides, sulfadimethoxine had highest adsorption affinity in pH range of 4.0-8.0. Their sorbilities were attributed to presence of different substitution group determining on their pK_a values.

Dual porosity model with physical non-equilibrium sorption depicted properly the transport of both conservative tracer and the reactive organic compounds, bromide and sulfonamides. Simulation with HYDRUS-1D showed that transport regime in the disturbed soil columns with sieved soil materials describe more physical equilibrium with more accessible sorption sites than the undisturbed soil columns. Physical non-equilibrium process in the undisturbed soil columns came from their heterogeneous soil structures. The heterogeneity also contributed to activate preferential flow, as given by modelling and bromide breakthrough curves. The preferential flow exhibited in the undisturbed soil columns therefore induced faster transport of the conservative tracer and the sulfonamides.

The column experiments performed under various pH conditions demonstrated that transport of the sulfonamides is pH-dependent in soil system. The dependency strongly reflects negatively charged species being inert to sorption sites on soil surface rapidly move through the soil columns. This is coincident with the findings obtained from the batch sorption experiments.

A large number of modelling programs has been developed over several decades to describe distribution of pollutants in environment. Release of various types of pharmaceuticals in agricultural region is an upcoming issue, and our findings can be a key knowledge concerning fate and transport of the acidic antibiotics in soils. However, influence their

mobility may be influenced by soil pH and soil constituents, such as natural organic carbon. The spatial heterogeneity of the soil structure also vary at field scale. Further investigations should be thus focused on effects of both physic-chemical properties of soils and the spatial heterogeneity at the field scale.

2.5 Acknowledgements

This study was supported by the Complex Terrain and Ecological Heterogeneity Project (TERRECO, WP 2-11) and DAAD (Deutscher Akademischer Austauschdienst) scholarship programme for doctoral candidates. We would like to acknowledge the International Environmental Analysis and Education Center (IEAEC) in Gwangju Institute of Science and Technology (GIST) for support of the sulfonamide analysis.

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Chapter 3

Transport of sulfonamide antibiotics in crop fields during monsoon season

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ABSTRACT:

Previous studies have documented the occurrence of veterinary sulfonamide antibiotics in groundwater and rivers located far from pollution sources, although their transport and fate is not relatively unknown. In mountainous agricultural fields, the transport behaviour can be influence by climate, slope gradient and physico-chemical properties of the sulfonamides. The objective of this research is to describe transport behaviour of 3 sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine) in sloped agricultural lands located in Haean catchment, South Korea. During dry and monsoon season, solute transport experiment was conducted in 2 typical sandy loam agricultural fields after application of the antibiotics and potassium bromide as conservative tracer. Observations and simulation of response to precipitation revealed that frequency and amount of runoff generation indicate a relation between slope gradient and rain intensity during monsoon season. Since slope influenced partitioning of precipitation between runoff and subsurface flow, higher loss of the sulfonamide antibiotics and bromide by runoff was observed at the higher sloped field. Bromide on topsoil was rapidly transported into subsurface at high infiltration rates. On the contrary, the sulfonamides were relatively retarded in the upper soil layer due to adsorption onto soil particles. Presence of furrows and ridges affected distribution of the sulfonamide antibiotics in

subsurface, due to horizontal water flow from ridges to furrows. Modelling results with HydroGeoSphere matched with background studies that describe physico-chemical properties of the sulfonamides, interaction between soil and the antibiotic group, solute transport through vadose zone and runoff induction by storm events.

Keyword: sulfonamide antibiotics, contaminant transport, ridge-furrow tillage, groundwater protection, HydroGeoSphere

3.1 Introduction

Occurrence of veterinary pharmaceuticals in environment are an emerging scientific issue (Brown et al., 2006; Kolpin et al., 2002). The active medical substances discharged with manure are washed off from agricultural soil, and move into aquatic system during precipitation. Various kinds of medicines released into the environment bring about adverse effects on aquatic and terrestrial organisms as well as on human beings, such as malfunctions in physiological systems and the induction of specific diseases (Sarmah et al., 2006). Moreover, pharmaceutical compounds are refractory to biodegradation in the environments, with half-life time ranging from months to years (Boxall, 2008).

Sulfonamide veterinary antibiotics are widely used in commercial animal feeding in order to prevent infectious diseases and to promote animal growth. In Korea, the purchased amount of the sulfonamides was about 240 tons in 2001 (Korea Food and Drug Administration, 2006), and 100 tons of the antibiotics were consumed in United Kingdom in 2004 (Veterinary Medicines Directorate, 2005). The antibiotics are frequently found across surface water, groundwater and soils. For example, extensive monitoring studies performed in German agricultural areas showed that a large number of soils and groundwater was contaminated by the sulfonamides residues (Hirsch et al., 1999; Höper et al., 2002). In the agricultural lands

fertilized with manure, the concentration of sulfadimidine were detected up to 11 μg/kg (Höper et al., 2002). Maximum concentrations of the sulfonamides in groundwater below the German crop land ranged from 0.16 μg/kg (sulfadimidine) to 0.47 μg /kg (sulfamethoxazole) (Hirsch et al., 1999). The wide range in concentrations indicate broad variability in input and transport process of individual sulfonamide antibiotics within vadose zone.

In general, the sulfonamide veterinary antibiotics are not fully metabolized by physiological processes in animal body, and the rest of active compounds are excreted through faeces and urine. Therefore, applying of manure collected from livestock farming is a highly relevant exposure route in agricultural regions. Recent investigations of the antibiotic pollution have raised scientific concern, since low levels of the antibiotics can lead to proliferation of antibiotic resistant microorganisms (Levy, 1997; NASCDUFA, 1999). The use of the sulfonamide antibiotics in livestock industry is linked to emergence of the resistant pathogenic strains which can be transferred from animals to humans (Lathers, 2002).

In previous laboratory-scale studies concerning pharmaceuticals, mobility, transport and distribution in environment is generally dependent on physico-chemical properties of the compounds (i.e. octanol-water distribution coefficient), soil characteristics and environmental situation. During heavy rainy season like summer monsoon, their transport behaviours may tend to vary greatly, depending on the precipitation and site characteristics. In mountainous agricultural regions, slope gradient plays an important role in partitioning of rain water between runoff and subsurface flow associated with pollutant transport. Due to the limited number of field studies, transport process of the sulfonamide antibiotics in sloped field is still unclear. Understandings of the pollutant transport is useful to improve strategies for controlling the antibacterial agents in agricultural areas.

The objective of this study was to depict transport and fate of selected sulfonamide

antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine) in two sloped agricultural land during monsoon season, in combination with field measurements and a numerical modelling, HydroGeoSphere. We hypothesized that removal of the sulfonamides by runoff would be higher in higher sloped field. In contrast, we hypothesized that their mobility in subsurface region would be enhanced in lower slope field during monsoon season. We also examined effect of their sorbility on distribution in subsurface and washout by runoff.

3.2 Materials and methods

3.2.1 Study area

The Haean catchment is located in North-eastern part of Gangwon Province in South Korea. Dryland farming is dominant in the hillsloped parts of the catchment, while rice cultivation is mostly practiced in the flat agricultural areas. The average precipitation is estimated as 1500 mm/yr, and 50-60 % of total annual precipitation is concentrated in summer monsoon from June to July. However, frequency and amount of rainfall increased from late July to mid-August, because withdrawal time for Changma has tended to be late in the recent decade (Ha et al., 2005).

The steep farmlands surrounding mountainous ridges are mainly covered with acidic and podzolic Cambisols formed from weathered metamorphic rock (Meusburger et. al, 2013). Due to high soil erosion caused by runoff generation during summer monsoon season, artificial additions of sandy soil are frequently used in order to compensate the soil loss. Therefore, the agricultural land management is strongly relevant to the fast pollutant leaching from top soil to adjacent soil horizons.

The field experiments was performed at two different potato fields (Rectangle, L: 8.0 m, W: 2.1 m) located on mountainous landslides within Haean catchment (N 38° 16', E 128°

8'; altitude 620 m). The fields were managed with ridge-furrow system, and the slope gradient of each field was 9.0° for Field A and 4.5° for Field B (Fig. 3.1). Soil properties of the experiment fields are shown in Table 3.1. No bedrock layer was not found within 10 m depth. 100mg of sulfamethoxazole, sulfadimethoxine and sulfamethazine (Sigma-Aldrich, Seelze, Germany) and 500g KBr (Merck, Darmstadt, Germany) were applied to top soil (depth: < 2cm) on May 20, 2011 in each field. Before applying the sulfonamides and bromide, seed potatoes, planted on 15 May were eliminated to prevent absorption of the antibiotics and the tracer by growing potatoes. During our field experiments (from 20 May to 10 June, 2011), typical characteristics of summer monsoon precipitation were observed as given in Fig. 3.1.

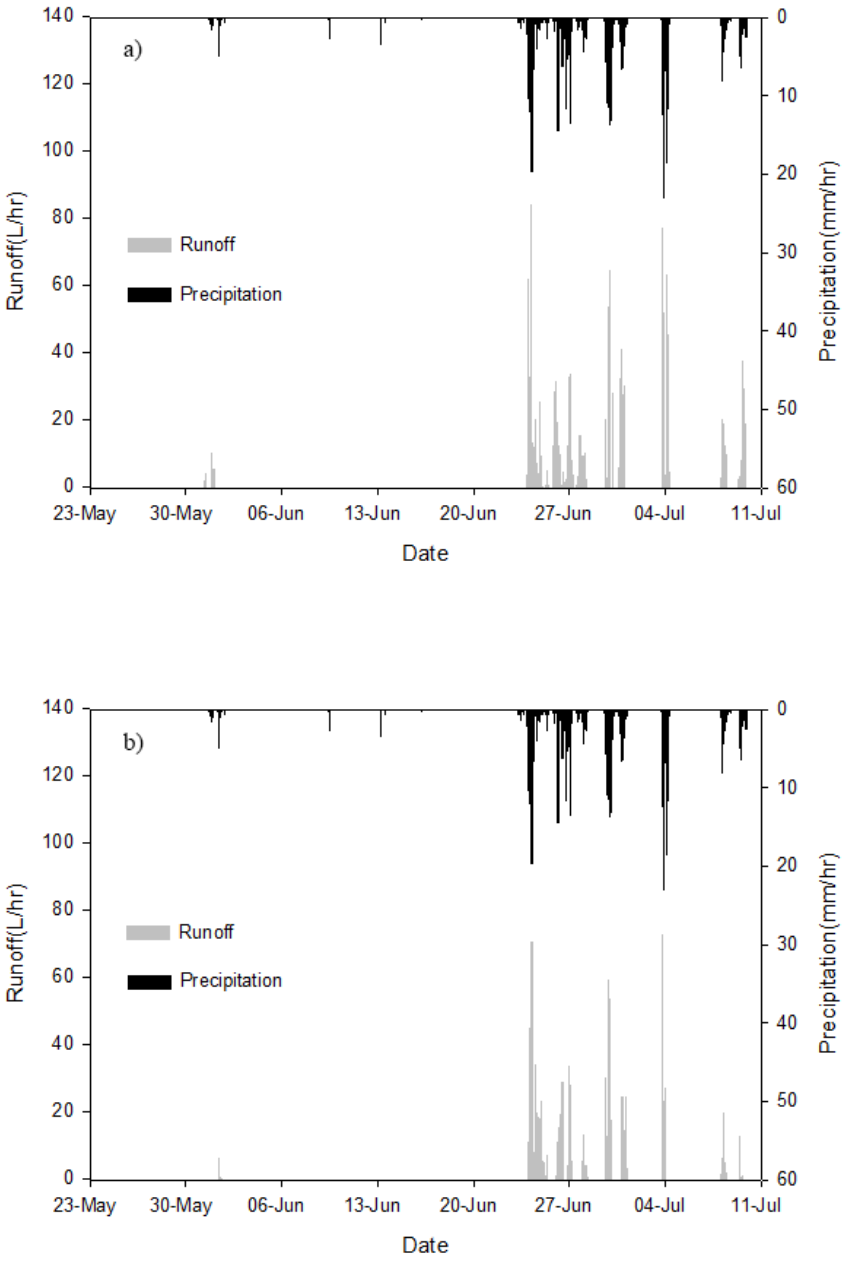


Fig. 3.1 Precipitation and runoff generation in research area, in period of experiment; a) field A, b) field B

Table 3.1 Soil properties of two fields

	Depth	Horizon (WRB)	Sand (%)	Silt (%)	Clay (%)	Bulk density (g/cm^3)	Organic carbon (%)	Soil texture (USDA)
Field A	0-30	Ap	71.5	20.2	8.3	1.42	3.61	Sandy Loam
	30-60	Bw	55.3	25.7	19.0	1.48	2.51	Sandy Loam
	60-100	Bwb	55.7	29.4	14.9	1.52	1.90	Sandy Loam
Field B	0-30	Ap	74.1	20.8	5.1	1.34	3.37	Sandy Loam
	30-60	Bw	53.1	28.1	18.8	1.47	2.48	Sandy Loam
	60-100	Bwb	52.9	32.5	14.6	1.58	1.77	Sandy Loam

3.2.2 Field measurement

Tensiometers and FDR sensors (Decagon 10HS moisture sensors, Decagon Devices Inc., Pullman, USA) were installed in two different sloped fields (Field A: 9.0°, Field B: 4.5°). In 2 furrows and 3 ridges of each field, the tensiometers were set up in depth of 20, 40 and 70 cm from surface of the furrows and ridges (Fig. 3.2). The difference of height between furrows and ridges was 15cm. In order to estimate amount of runoff, multislot divisors and pressure sensors were adapted using a stationary slotted crown (Arnhold et al., 2013). The crowns were equipped on the top of 20L plastic bucket. When the first bucket was filled with runoff, a small fraction of water moved into second bucket. The data from FDR sensors and pressure sensors were automatically collected using Em50 Digital/Analog Data Logger (Decagon Devices, Inc., Pullman, USA) and Delta T-logger (Delta-T Devices Ltd., Cambridge, United Kingdom). Suction candles designed to collect soil-water were also installed in depth of 20, 40 and 70cm from surface. After rain events, they moved into freezer to prevent degradation of target

pollutants. Runoff was also collected in front of multislot divisors.

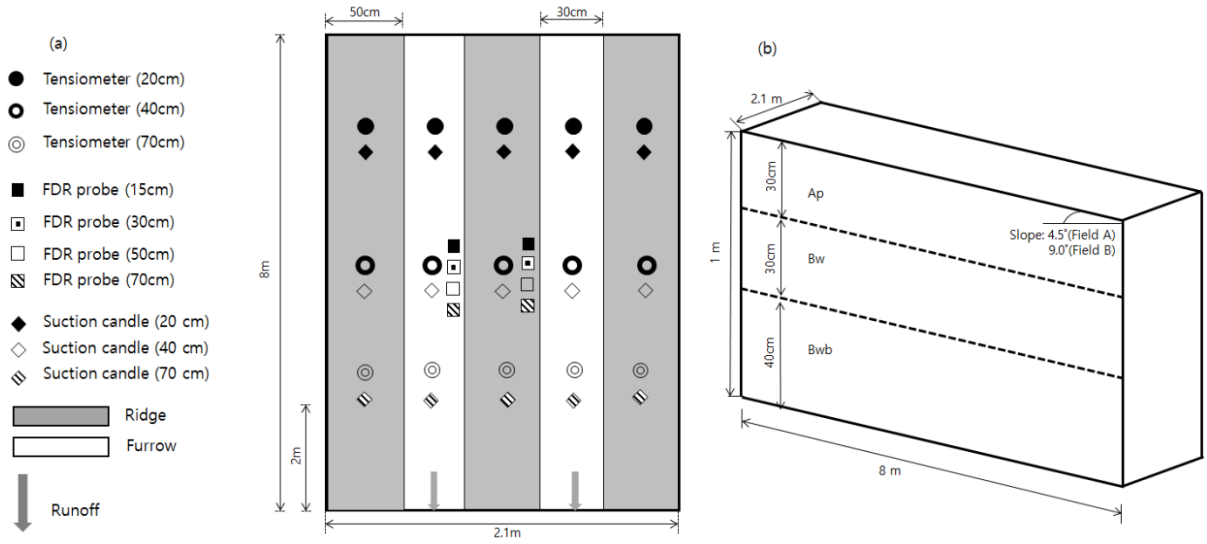


Fig. 3.2 Schematic illustration of experiment fields: (a) for measurement facilities installation (b) for soil layer.

3.2.3 Analysis of antibiotics

The target sulfonamides in water and soil samples were analyzed using high-performance liquid chromatography with mass spectrometry (Waters, Quattro micro TM API, Milford, MA). Sulfamethoxazole-D_4, sulfadimethoxine-D_4 and sulfamethazine-D_4 (Toronto Research Chemicals Inc., North York, Ontario, Canada) were used as internal standard. 20ml water sample was filtered through a 0.22μm PES membrane (Millipore, Billerica, MA) to separate suspended particles in sample. The used filters were sonicated in 5ml methanol (Th. Geyer GmbH, Renningen, Germany) for 30 minutes in order to extract adsorbed antibiotics onto suspended particles, and then the extract was dissolved in 200ml deionized water to reduce the solvent effect. Through solid phase extraction (SPE) using OASIS HLB cartridge (Waters, Milford, MA), target antibiotics were more concentrated in 1ml extraction (acetonitrile: water, 3:7).

3.2.4 Modelling set up

In order to depict water and the chosen solute transport, surface and subsurface processes should be integrated with precipitation and evapotranspiration. The processes can be investigated in the context of the finite element method, HydroGeoSphere, a fully-integrated 3D surface/subsurface model considering precipitation and evapotranspiration. HydroGeoSphere is capable simultaneously to simulate water flow and advective-dispersive solute transport of the overland flow (2D) and of subsurface flow (3D) under variably-saturated conditions.

HydroGeoSphere explicitly uses the overland flow domain as a layer on top of the subsurface domain. That is to say, the node of overland flow domain shares to top of the subsurface domain. To consider topographic variations for overland flow, concept of rill storage are implemented in HydroGeoSphere. The overland flow parameters for rill storage, rill storage height and coupling length were set to 1 cm, as given in previous study performed in same region (Ruidisch et al., 2013).

The fields consisted of three subsurface zone with different properties. As shown in Table 3.1, the topsoil extended 30cm below the surface, and second zone was between 30 cm and 60cm below the surface. The last zone was occupied from 60cm to 100cm below the surface.

3.2.5 Governing Equations

In HydroGeoSphere, solute transport is coupled with surface-subsurface water flow. Surface water flow is considered by two-dimensional Saint Venant equation with diffusion wave approximation.

$$-\nabla \cdot (d_o q_o) - q_o \Gamma_o \pm Q_o = \frac{\partial}{\partial t}(\theta_o h_o)$$

where the surface water flux q_o (LT^{-1}) is given by

$$q_o = -K_o \cdot L_a \nabla (d_o z_o)$$

where θ_o is a surface flow domain porosity which is unity for flow over flat plane. d_o is the depth of flow (L), z_o is the land surface elevation (L), and h_o is the water surface elevation ($h_o = z_o + d_o$). K_o is the surface conductance (LT^{-1}), Q_o is the surface water source or the sink ($L^3L^{-3}T^{-1}$), and Γ_o is the surface water exchange rate with subsurface domain ($L^3L^{-3}T^{-1}$). L_a (-) is a factor accounting for the reduction in horizontal conductance from obstruction storage exclusion.

Modified Richards' equation is applied to compute subsurface water flow, as follow:

$$-\nabla \cdot (w_m - K \cdot k_r \nabla (\varphi + z)) + \sum \Gamma_{ex} \pm Q_u = w_m \frac{\partial}{\partial t}(\theta_s S_w)$$

where w_m (-) is the volumetric fraction of the total porosity occupied by porous medium. K is hydraulic conductivity tensor (LT^{-1}), and k_r (-) is the relative permeability of subsurface. φ is the pressure head (L), and z is elevation head (L). Γ_{ex} represents the volumetric fluid exchange rate between the subsurface domains. S_w (-) is water saturation related to the water saturation content θ_s (-). Q_u represents subsurface water source or sink ($L^3L^{-3}T^{-1}$).

Water exchange fluxes are estimated in the conductance concept coupling. The exchange term is given by:

$$d_o \Gamma_o = \frac{k_r K_{zz}}{l_{ex}}(h - h_o)$$

Where Γ_o is flow from the subsurface system to the surface system ($L^3L^{-3}\,T^{-1}$), h_o is the surface water head (L), and h is the subsurface water head (L). k_r is the relative permeability

for the exchange flux (-), K_{zz} is the vertical saturated hydraulic conductivity of the porous medium (L T^{-1}) and l_{ex} is the coupling length (L).

The transport process of solute considering advection, dispersion, sorption, and degradation in porous media is depicted by the following equation:

$$-\nabla \cdot w_m(qC - \theta_s S_w D\nabla \mathrm{C}) + (w_m \theta_s S_w R\lambda C) + \sum \Omega_{ex} \pm Q_c$$

$$= w_m[\frac{\partial}{\partial t}(\theta_s S_w RC) + (\theta_s S_w R\lambda C)]$$

where C is the solute concentration (ML^{-1}), and λ is a first-order degradation rate (L^{-1}). Ω_{ex} is the mass exchange rate of solute per unit volume ($ML^{-3}T^{-1}$) between surface and subsurface domain, and Q_c represents the water source or sink ($ML^{3}T^{-1}$). ω_m is the subsurface volumetric fraction of the porosity (-), q represents the subsurface water flux (LT^{-1}), and D is hydrodynamic dispersion tensor of subsurface domain ($L^{2}T^{-1}$). R is the retardation factor related to sorption of the solute:

$$R = 1 + \frac{\rho_b}{\theta_s S_w} K_f$$

where ρ_b is the bulk density of the porous media (ML^{-3}), and K_f is equilibrium distribution coefficient describing a linear Freundlich isotherm ($L^{-3}M$). The hydrodynamic dispersion tensor D is given by:

$$\theta_s S_w D = (\alpha_l - \alpha_t)\frac{qq}{|q|} + \alpha_t |q| I + \theta_s S_w \tau D_f I$$

where α_l and α_t are the longitudinal and transverse dispersivities (L). |q| is the magnitude of the Darcy flux, and τ is the matrix tortuosity (-). D_f represent free-solution diffusion coefficient for the matrix ($L^{2}T^{-1}$). The product, τ D_f is an effective diffusion coefficient for the matrix.

3.2.6 Initial and Boundary condition

The initial pressure head conditions in the subsurface domain were set to measured pressure head using the tensiometers. The water and solute transport started on the application day of the sulfonamide antibiotics and bromide on top soil (23 May, 2011). Since the sulfonamide antibiotics were applied only on the top soil layer, the initial concentrations of each sulfonamide were defined for the upper 2cm depth from surface, and initial concentrations for rest of subsurface domain were zero. The bottom boundary of the fields was set to free drainage boundary, since groundwater table was found 30m below the surface. The lateral boundary was set to zero-flux boundary due to block panels inserted around subsurface region.

3.2.7 Model parameterization and parameter optimization

In order to determine hydraulic and solute transport parameters using inverse modelling, HydroGeoSphere was coupled with a parameter optimization tool, Parallel PEST (Version 12.1.0). The nonlinear parameter estimation is adapted to Gauss-Marquardt-Levenberg algorithm in determining the optimum upgrade vector. Parallel-PEST can repeat determination of the parameter upgrade vector with further parameters held fixed. Based on soil texture, initial values of the Van Genuchten parameters was obtained using Rosetta Lite (version 1.1) implementing hierarchical pedotransfer functions for the estimation of water retention.

Values of longitudinal dispersivities were estimated between 0.01m and 0.5m in accordance with findings of previous study (Gelhar et al., 1992). The review by Gelhar et al. (1992) showed that the longitudinal dispersivities range from 10^{-2}m to 10^{4}m for scales ranging from 10^{-1} to 10^{5}m. According to Marsily (1986), transverse dispersivity of porous media is commonly 0.01 to 0.2 of longitudinal dispersivity. Therefore, initial values of transversal and

vertical transversal dispersivity were set to 0.001m, and then they were optimized in a range from 0.0001m to 0.01m. Since the sulfonamide antibiotics was sorbable onto soil and non-volatile, the volatilization process was ignored. Adsorption coefficients (K_d) of the sulfonamides and bromide estimated from our batch sorption experiment were used for retardation factor. Diffusion coefficient of the sulfonamides was calculated using Stokes-Einstein equation based on molecular weight. Degradation rate of the sulfonamide antibiotics in soil and soil-water system is low under both aerobic and anaerobic condition (Kunkel and Radke, 2008; Radke et al., 2009). For parameter estimation, we used initial degradation rate suggested by previous study (Radke et al., 2009).

In order to evaluate the model, relative coefficient (R, R^2) and Nash-Sutcliffe efficiency (NSE) were estimated (Nash and Sutcliffe, 1970). The coefficient of determination is between 0 and 1.0. The NSE is a normalized measure which compares the mean square error generated by a hydrological simulation to the variance of the target output sequence. The value is calculated as follow;

$$\mathrm{NSE} = 1 - \left[\frac{\sum_{i=1}^{n}(Y_i^{obs} - Y_i^{sim})^2}{\sum_{i=1}^{n}(Y_i^{obs} - Y_i^{mean})^2}\right]$$

where Y^{mean} is the mean of the observed dataset, Y_i^{obs} indicates *i*th observation of the observed and Y is the *i*th observation of the modelling dataset, *n* is the total number of observations. The range of NSE lies between - ∞ and 1.0. NSE value = 1.0 indicates perfect model performance, and an NSE value <0 indicates model performance is unacceptable.

3.3. Results and Discussions

3.3.1 Precipitation and runoff

Typical monsoon rains were observed during the experiment (Fig. 3.1), Strong rain events from 24 June to 10 July resulted in both surface runoff and water seepage into soil layer. From 24 June, several strong rain events were observed up to 126mm/day, and the hourly intensity of rainfall varied from 0 to 23mm/hr. Runoff generation was dependent on rain intensity for whole experiment period. Slope of the experiment fields also affected runoff. Compared to Field B, runoff generation from Field A was more frequent, and also the amount of runoff generation was relatively high (Field A: 0 – 84.18 L/hr, Field B: 0 – 70.42 L/hr). After starting rainy season (24 June), even low precipitation generated surface runoff on both fields, since the water content of subsurface region was higher than during dry season (23 May – 23 June). From 2 June to 23 June, no runoff was generated even though two rain events were occurred due to low intensity and amount of precipitation.

As shown in Fig. 3.3 and from calculated Nash-Sutcliffe efficiencies (Field A: 0.83, Field B: 0.79), the comparison between simulated and observed surface runoff showed a good agreement for both fields, whereas the results for field B were less satisfying. The runoff generation in dry season was simulated reasonably well, but the model underestimated runoff generation in monsoon season.

Table 3.2 Nash-Sutcliffe efficiency (NSE), Pearson's correlation coefficient (R) and correlation of determination for Runoff generation (R^2)

	NSE	R	R^2
Field A	0.83	0.92	0.85
Field B	0.79	0.90	0.82

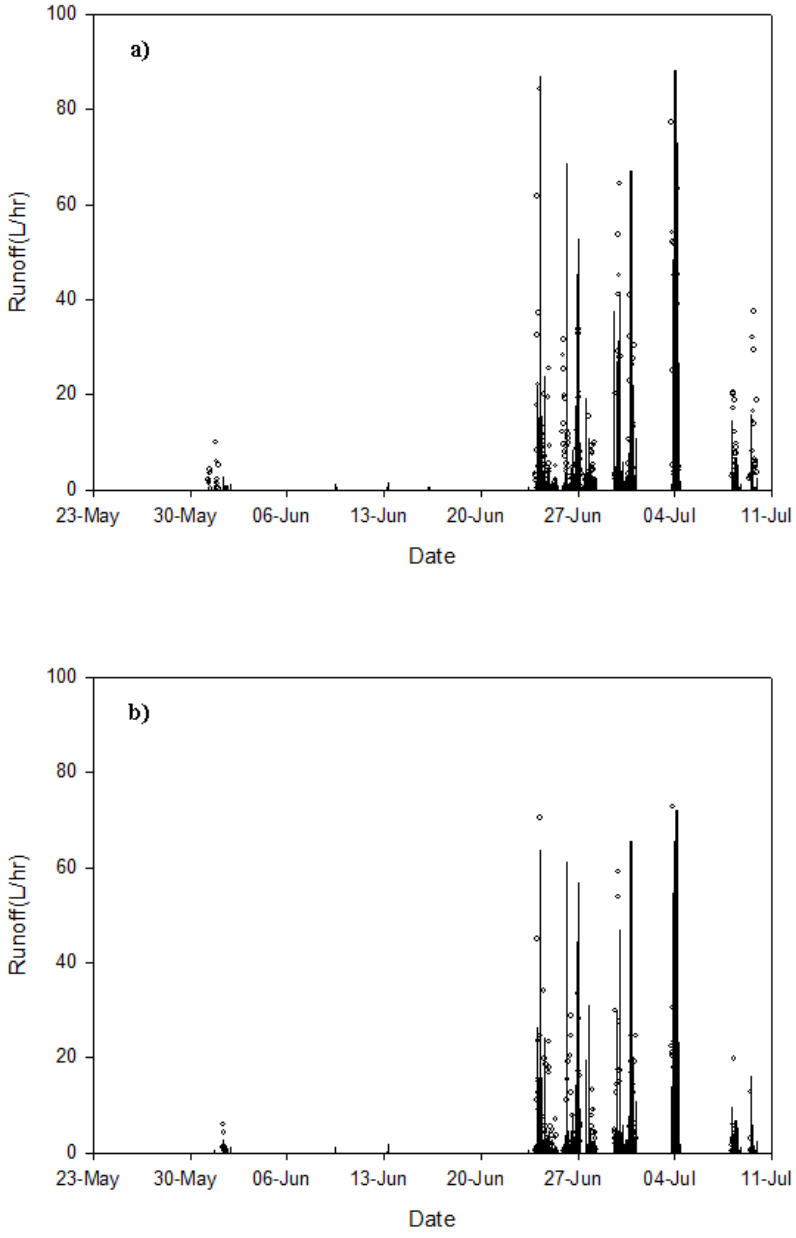


Fig. 3.3 Simulated and observed runoff generation; a) field A, b) field B (solid bar: simulated runoff, open dot: observed runoff)

On hillside region, runoff generation is strongly dependent on the shape of the surface, soil texture and slope (Chaplot and Bissonnais, 2003; Assouline and Ben-Hur, 2006). The texture of the soils of both agricultural field sites was sandy loam, and had the same ridge-furrow system on the surface. In general, runoff generation is driven by the soil moisture level exceeding vertical infiltration rates. As slope increases, the vertical infiltration rates were significantly reduced. Therefore, it is obvious that the difference of runoff generation was associated with the slope values.

3.3.2 Bromide and sulfonamide antibiotics in runoff

Concentration of the target antibiotics and conservative tracer (Br^-) in runoff varied between two fields, due to runoff generation and slope of the observed fields. As the sulfonamide antibiotics and bromide existed only in top soil (≤ 2cm), they were easily washed out by first rain event on 31 May. After starting intensive precipitation on 23 June, concentrations of bromide were detected in very low. Owing to very low adsorption on soil material, the conservative tracer was partitioned rapidly into deeper layer and runoff at beginning of the rainy season.

As shown in Fig. 3.4 and 3.5, high concentration of the sulfonamide antibiotics were observed in runoff generated by precipitation on 31 May. Concentration of the antibiotics decreased during the strong precipitation like bromide. Compared to bromide, decrement of the antibiotics concentration was relatively low. The difference may be induced by higher sorbility of the sulfonamide antibiotics to soil, especially top soil layer within 2cm where runoff generation and solute exchange occurred. In batch sorption experiment for adsorption coefficient (K_d), the estimated value of chosen antibiotics was about 500-fold higher than bromide, at least. In contrast, behaviour among the sulfonamide antibiotics in runoff was not significantly different. The antibiotics concentrations were fluctuated during the heavy rain

event. The rain intensity varied, and soil loss caused by runoff corresponded to the rain intensity in the agricultural lands. The chosen antibiotics adsorbed onto soil particle were transported by runoff. The above result implies that the sulfonamide movement by runoff is a typical particle facilitated transport.

As given in Fig. 3.4 and 3.5, simulation of the antibiotics transport with HydroGeoSphere has a good agreement with measured values. Nevertheless, the transport model underestimated washout of the applied sulfonamides by runoff, especially during monsoon season. Although HydroGeoSphere is fully integrated modelling program for water flow and solute transport, the model cannot consider soil erosion and particle facilitated transport, which is one of important transport mechanism during the strong rain event generating loss of soil particles.

Concentrations of the antibiotic in runoff were not different among the applied sulfonamide in the whole experiment, except in first runoff (31 May). The precipitation on 31 May lead to fast movement of the applied sulfonamides into subsurface region. In accordance with the modelling and analytic result, distribution among the sulfonamide antibiotics was similar within upper soil layer (<10cm), where solute exchange was actively occurred between runoff and subsurface flow. This finding also suggests that nonequilibrium sorption processes were dominant on top soil layer in the whole period.

In the present study, slopes of the fields significantly effected on transport of the sulfonamide antibiotics and bromide by runoff. From Fig. 3.4 and 3.5, it appears that the sulfonamide concentrations in runoff from Field A were higher than from Field A during the whole period. During rainy season staring on 23 June, bromide concentrations from Field A were also relatively higher. The difference of runoff generation was responsible for the large difference in the concentration of the sulfonamide antibiotics and bromide.

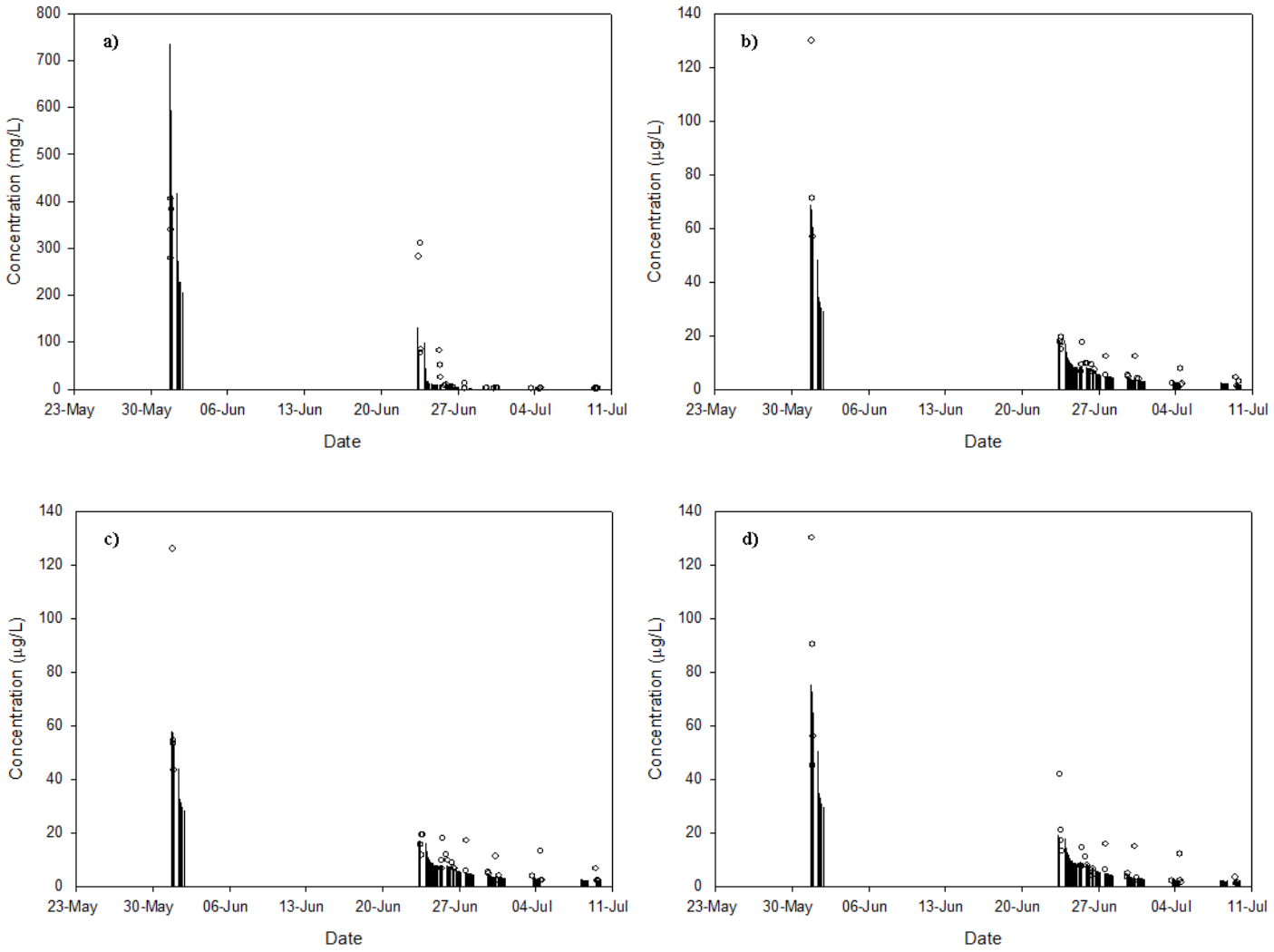


Fig. 3.4 Concentration of Br, sulfamethoxazole, sulfadimethoxine and sulfamethazine in runoff from Field A; a) Bromide, b) Sulfamethoxazole, c) Sulfadimethoxine, d) Sulfamethazine (solid bar: simulated runoff, open dot: observed runoff)

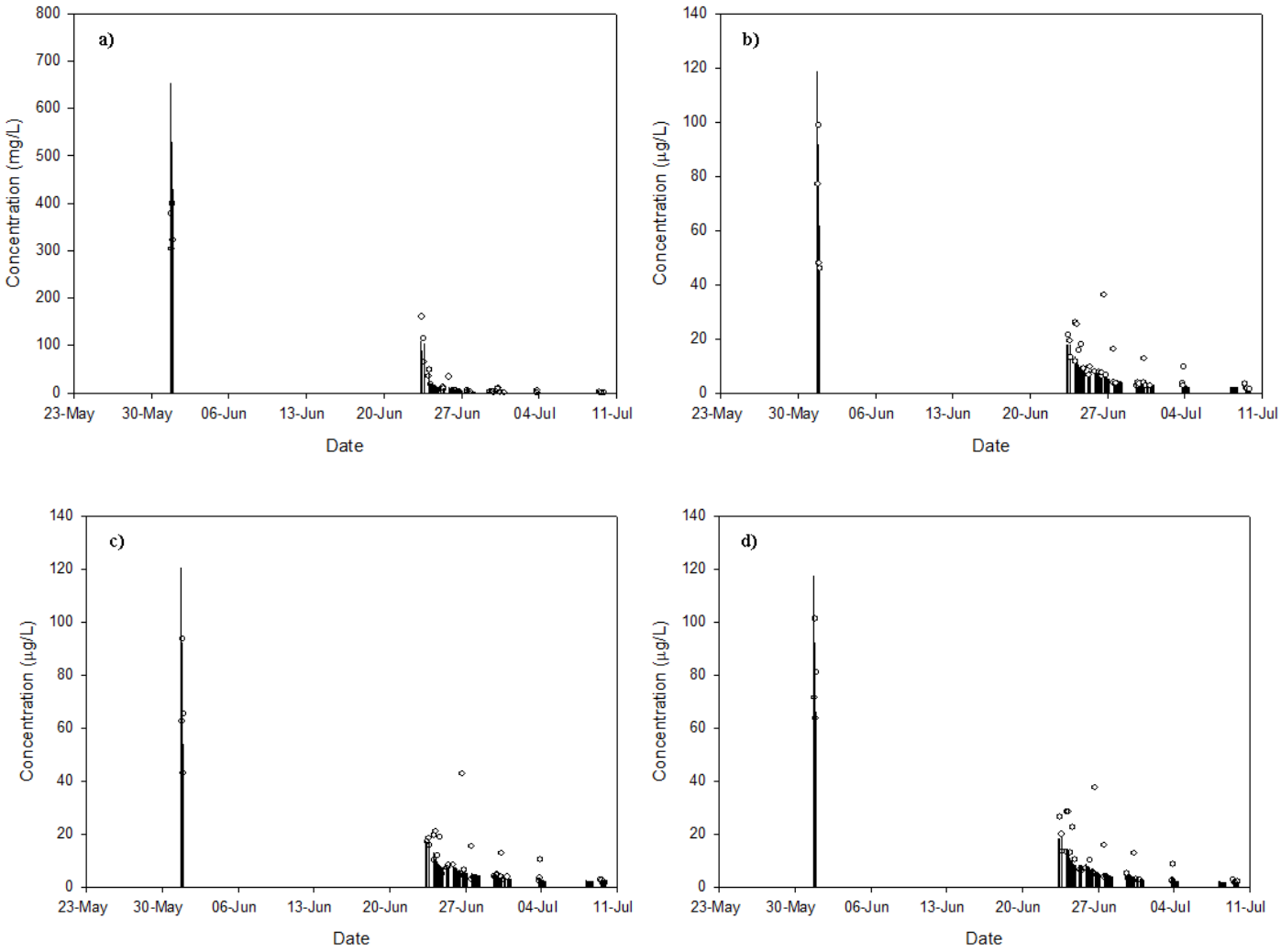


Fig. 3.5 Concentration of Br, sulfamethoxazole, sulfadimethoxine and sulfamethazine in runoff from Field B; a) Bromide, b) Sulfamethoxazole, c) Sulfadimethoxine, d) Sulfamethazine (solid bar: simulated runoff, open dot: observed runoff)

3.3.3 Transport of bromide and sulfonamide antibiotics in soils

In this study, bromide has been applied on top soil (0-1cm) as conservative tracer to describe water flow in the experiment field. In order to confirm background level of Br, 1m soil column was taken, and was estimated natural-born bromide. No bromide was detected in whole top and subsurface layer before bromide application. As shown in Fig. 3.6, 3.7, 3.8 and 9, detection of the bromide tracer in soil-water exhibited a considerable spatial variability, after precipitations were observed. From surface, concentrations of the conservative tracer decreased toward deeper layer on 30 May. The other two rain events occurred before monsoon season also transported the bromide from the top layer into deeper soil layer, but the distribution changed a little, due to low precipitation rate. During the heavy rainy season, distribution of the bromide changed in subsurface, and rapidly moved into deeper soil layer. The transport pattern of bromide indicates that water flow in subsurface region was very fast during the rainy season. This coincides with high hydraulic conductivity and other Van Genuchten parameters estimated by Parallel-PEST.

Compared to the conservative tracer, transport of the sulfonamide antibiotics was relatively retarded in soil during whole experiment period. Most amount of the applied antibiotics existed in upper soil layer (≤ 10cm), and was not detected in depth of 40cm and 70cm until 23. June. During the dry season, concentration of the sulfonamides decreased as depth of the subsurface area. After starting the rainy season, the applied antibiotics was rapidly penetrated in subsurface region. The high water infiltration drove fast transport of antibiotics into deeper subsurface region, regardless of runoff generation. Fig. 3.6, 3.7, 3.8 and 3.9 show that transport of sulfadimethoxine was relatively retarded in upper soil layer, comparing other target sulfonamides. The results from modelling and chemical analysis indicate that distribution and transport of the sulfonamide antibiotics in subsurface is dependent on their

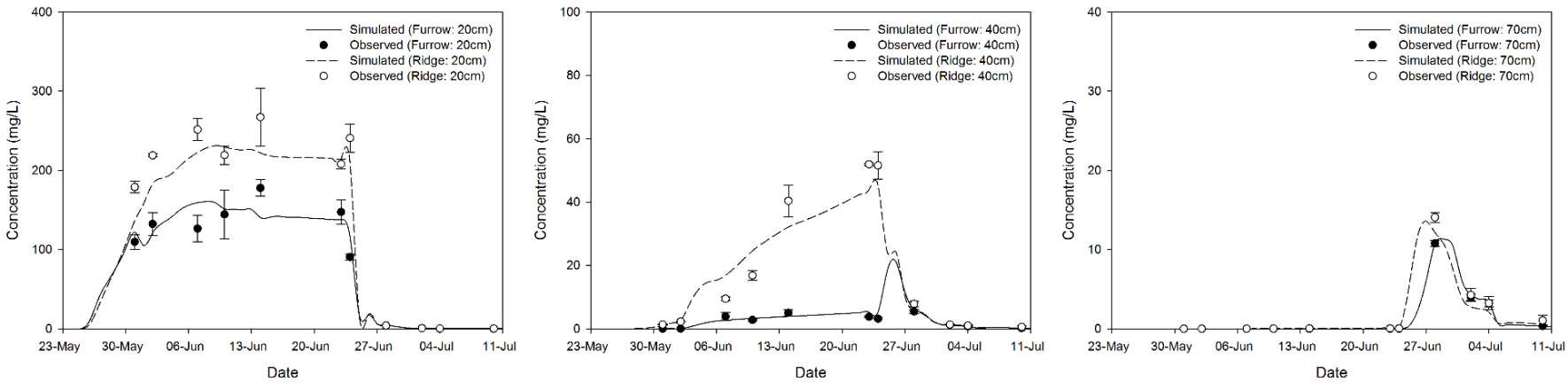
sorbility (K_d).

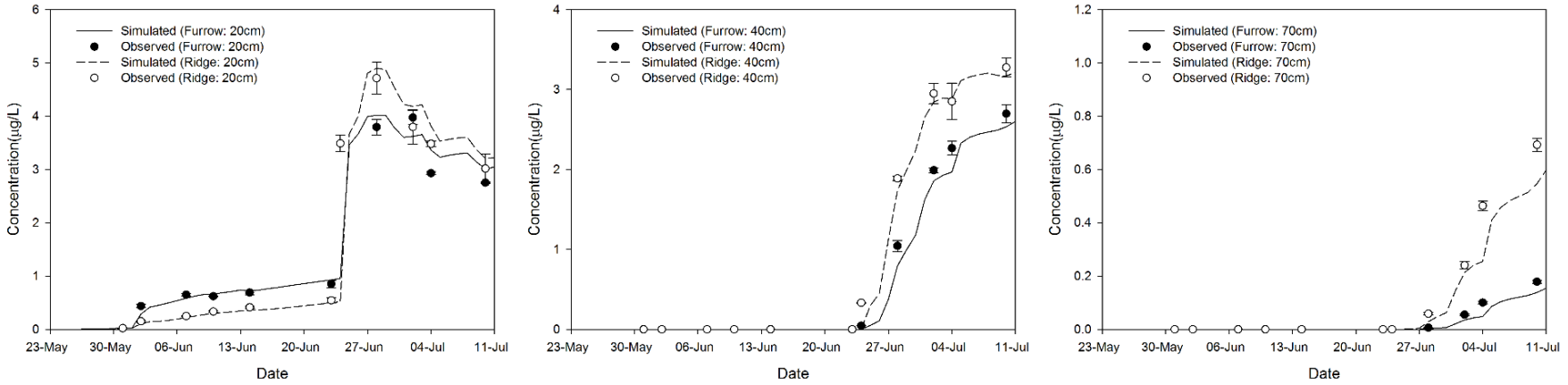
The ridge-furrow system used in this study affected water movement in the soil layer (Fig. 3.6, 3.7, 3.8 and 3.9). The topological characteristics caused different pressure head between ridge and furrow area. At Field A, pressure heads between ridge and furrow differed between -20 to -120cm, while difference in pressure heads were about -10 to -160cm at Field B. Although pressure head gradient was vertically higher at both fields (Field A: -7cm to -316cm, Field B: -3cm to -319cm), the horizontal different gradient partially drove soil water movement from ridge to furrow. During monsoon season, difference between vertical and horizontal pressure head gradient was significantly reduced due to strong precipitation. This leaded to transport of the applied sulfonamide antibiotics from furrow to ridge. Therefore, the different distribution of sulfonamide antibiotics was responsible for ridge-furrow system.

As shown Fig. 3.6, 3.7, 3.8 and 3.9, slope of the fields also effected on distribution of the sulfonamide antibiotics in subsurface region. For distribution of the sulfonamide antibiotics in subsurface, no significant difference was observed between the fields before monsoon season, and all sulfonamide antibiotics were detectable only top soil layer above 20cm depth. The difference in the residual concentration of the all sulfonamides between the fields became apparent below 70cm depth during monsoon season. At 70cm depth of Field A, residual concentration of sulfadimethoxine increased up to 1.90μg/L. Under the rainy period, higher concentration of sulfadimethoxine (0-0.32μg/L) were detected at same depth of Field B, due to relatively higher water infiltration rate.

For the solute transport, the simulation with HydroGeoSphere had a good agreement with measured values. Nevertheless, the structured modelling underestimated transport of the sulfonamide antibiotics and the conservative tracer. In general, tillage changes soil structure in

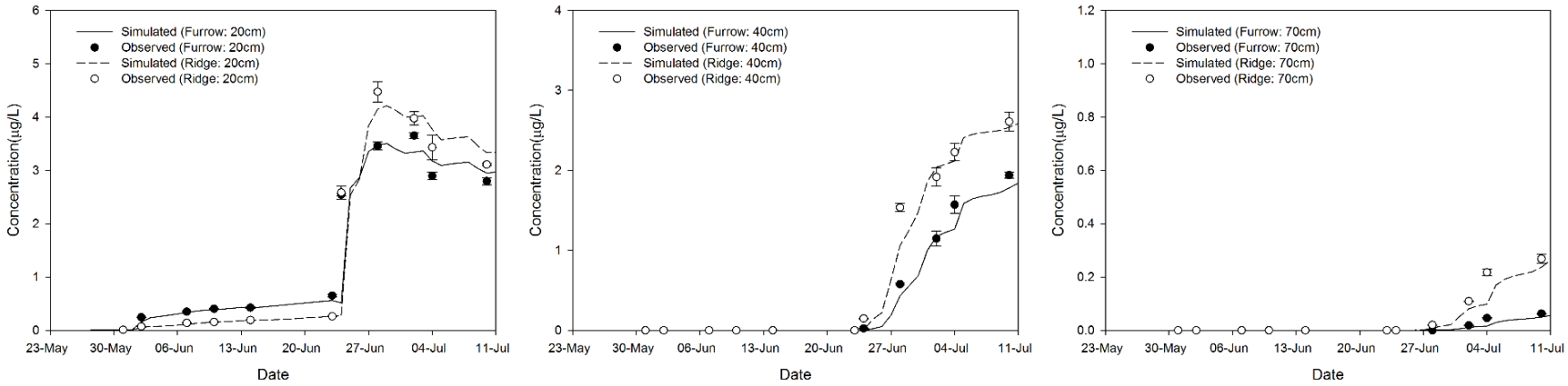
top soil layer, which would be important for generation of preferential flow (Petersen et al., 1999; Elliott et al., 2000). There was also considerable earthworm activity which is expected to make tunnels for preferential flow. Several studies have reported that rapid transport of solute is associated with preferential flow (Larsson et al., 1999; Zheng and Gorelick, 2003). Consequently, chemical composition of preferential flow strongly reflects to concentration of soil-water and overland flow near surface.





<Sulfamethoxazole>

Fig. 3.6 Concentration of Br and sulfamethoxazole in subsurface region of Field A



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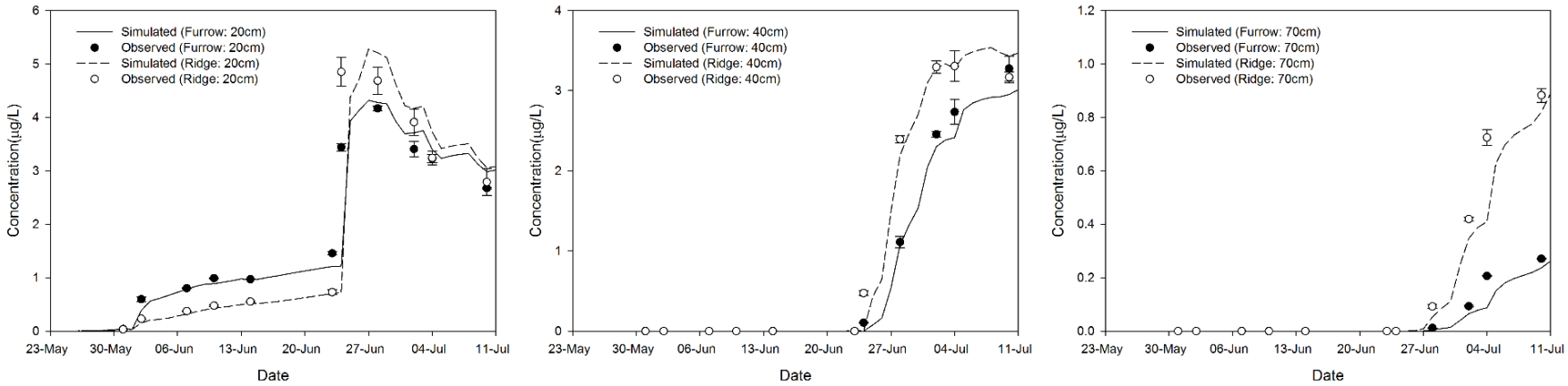
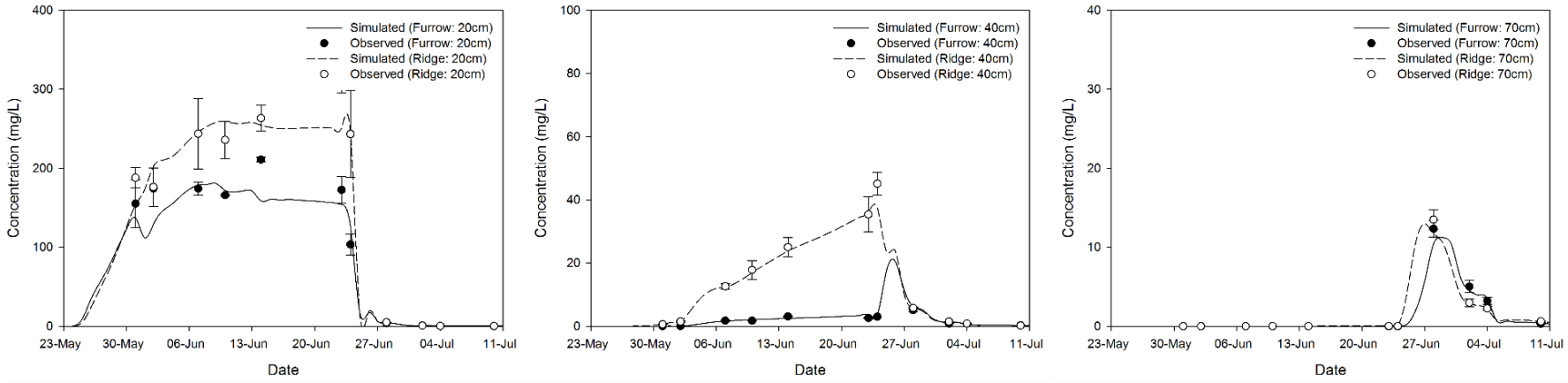


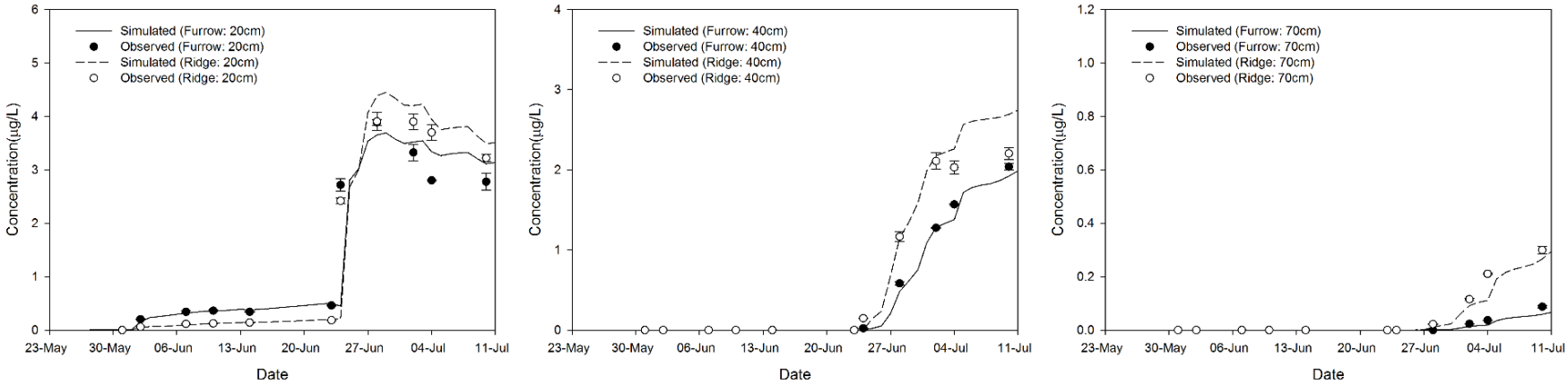
<Sulfamethazine>

Fig. 3.7 Concentration of sulfadimethoxine and sulfamethazine in subsurface region of Field A

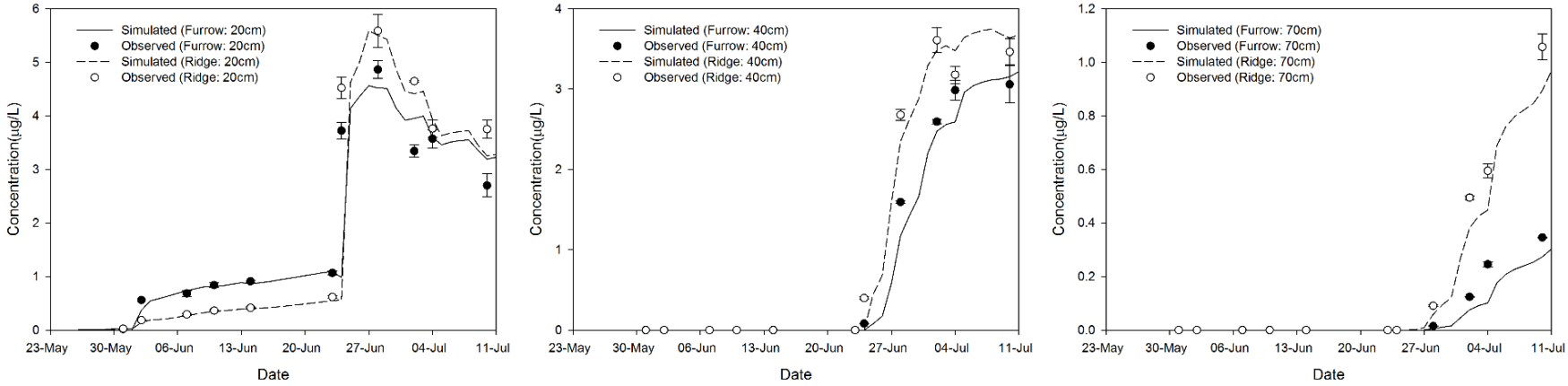


<Sulfamethoxazole>

Fig. 3.8 Concentration of Br and sulfamethoxazole in subsurface region of Field B



<Sulfadimethoxine>



<Sulfamethazine>

Fig. 3.9 Concentration of sulfadimethoxine and sulfamethazine in subsurface region of Field B

3.4 Conclusions

In this study, we performed field studies and model based analyses with HydroGeoSphere to investigate transport behaviour of the sulfonamide antibiotics and bromide during dry and monsoon season. High sloped area generated easily runoff, since partitioning of precipitation into subsurface flow decreased as increasing slope. This lead to higher loss of the sulfonamide antibiotics and bromide by runoff under the rainy season. The model has a good agreement with measured concentrations of the sulfonamide antibiotics in the runoff, whereas runoff of the sulfonamide antibiotics induced by first rain event was underestimated. In the simulation, the underestimation of the sulfonamides loss by runoff suggested that particle-facilitated transport may be a key transport mechanism in agricultural fields. Further understanding of the transport processes involving soil particles should come from combination with detailed experimental and modelling studies.

At both test field, the sulfonamide antibiotics moved rapidly into subsurface region during monsoon season. Before the rainy period, most amount of the sulfonamide antibiotics remained within topsoil layer (<20 cm depth), while non-adsorbable tracer, bromide penetrated fast into subsurface. Due to lower water infiltration caused by a higher slope gradient, all applied sulfonamide antibiotics and bromide in Field B were transported faster into the deeper soil layer than in Field A. Our simulation properly described distribution of the sulfonamides and bromide in subsurface, although their transport was underestimated during monsoon season, implying existence of preferential flow. The understandings and characteristics of sulfonamide transport need to be incorporated into other hydrological models to depict their toxicological issues in catchment and watershed level.

3.5 Acknowledgments

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3.6 References

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Chapter 4

Sulfadimethoxine transport in soil columns in relation to sorbable and nonsorbable tracers

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ABSTRACT:

In this study, miscible displacement experiment and batch sorption experiments were performed with sulfadimethoxine, dye tracer (Brilliant Blue FCF) and a conservative tracer (bromide) to depict, analyse and interpret transport paths of sulfadimethoxine in undisturbed and disturbed soil columns. Batch sorption experiment revealed that sorbility increased in the order: BB > sulfadimethoxine > bromide. The horizontal spatial patterns of sulfadimethoxine and the tracers were analysed in each depth, and selective samples were taken in horizontal cross-section. Non-adsorbable and conservative tracer, bromide spread more widely into longitudinal and horizontal direction than sulfadimethoxine and BB, since adsorption reduced transversal dispersion of the sulfadimethoxine and dye. In non-stained area, residual concentrations of sulfadimethoxine were relatively lower than in stained areas. Therefore, BB distribution can be used to approximate sulfadimethoxine movement in soil. However, presence of preferential flow networks found in undisturbed soil cores can enhance mobility of sulfadimethoxine and the tracers, due to faster flow velocities and non-equilibrium adsorption. Our findings showed that other dye tracers may also be applicable to identify transport pathways of various organic contaminants, of which physico-chemical properties are similar to those of the dye tracers. Preferential flow should be considered for drinking water managements and transport modelling, since this allows faster pollutants transport from their sources, and create critical consequences for groundwater quality and solute transport

modelling.

Keyword: sulfadimethoxine, pollutant transport, tracers, preferential flow

4.1 Introduction

Solute transport in soil is known a critical environmental key process, as various organic and inorganic pollutants are found in groundwater and soil-water systems, and thus posing a threat to drinking water. Several studies have been shown that the contaminated water can bring about adverse effects on the human health and terrestrial ecosystem functioning (Hartley et al., 1999; Anawar et al., 2002; Patrick et al., 1987). In order to estimate transport of pollutants in environmental matrices, various studies have focused on developing reliable tracing methods for water flow in soil and groundwater.

Study on contaminant transport in soil and ground water is still a demanding task. The difficulty is to be mainly caused by the complexity of the subsurface region, bringing about spatial and temporal variation of pollutant transport in soil and soil-water. Water flow in heterogeneous hierarchical soil structure generally accelerate movement of contaminants towards the groundwater. Preferential flow in burrows, fractures and wormholes together with nonlinear sorption can clearly related to rapid movement of water and pollutants in vadose zone (McCarty and Angier, 2001; Polyakov et al., 2005; Carlyle and Hill, 2001). However, detailed knowledge of quantitative relation between water flow and solute transport in rapid flow systems is still limited.

Pharmaceuticals have been released into environmental matrices, and the medical active compounds may potentially cause adverse effects on terrestrial and aquatic ecosystem (Fent at al., 2006; Kümmerer 2008). In particular, most of antibiotics are strongly resistant to be degraded by microorganisms in environment, and consequently they remain in the

environment for a long time (Boxall, 2008). Manure containing anthropogenic antibiotics has been widely applied to agricultural lands as fertilizer. As a major of veterinary antibiotics in medical market, sulfadimethoxine are used in livestock industry in order to prevent infectious diseases. Most amount of applied sulfadimethoxine enters into environment without chemical transformation in body. Owing to strong resistance against biodegradation by microorganisms, residues of the antibiotics is easily infiltrated into subsurface region, and eventually can reach to ground water and aquifer. Several studies have been reported occurrence of the sulfonamide antibiotics in the ground water, river bed and reservoir (Luo at al., 2011; García-Galán at al., 2011). Nowadays, conclusive information on the fate and transport of the sulfonamides in environment is just available for a few specific conditions (Srivastava et al., 2009; Vithanage et al., 2014; Zhang et al., 2014).

So far, with current knowledge and limited transferability of laboratory findings of their transport in soils, it is difficult to quantitative describe their behaviour in specific soil systems. Furthermore, even in the previous findings showing their transport characteristics in soil columns using in combination with breakthrough curves and inverse model, it has been difficult to present their transport pathways in complex soil structure. The antibiotics analysis is moreover expensive and time-consuming. For water flow in soil layers, distribution of dye tracers can be measured, and provides opportunities to identify transport processes and parameters (Aeby et al., 2001; Forrer et al., 1999). Main purpose of our study is to investigate sulfadimethoxine transport pathways in soil using colour dye (Brilliant blue FCF) and bromide. In this study, we hypothesized that the sorbable dye tracer can be used as a surrogate to describe combined effect of sorption and water flow pathway on the sulfonamide transport. Batch sorption experiment was performed to estimate sorbility of tracers. The effect of soil structure and adsorption of tracers on the target antibiotics movement was also identified in both disturbed and undisturbed soil columns with image processing and chemical analysis.

4.2 Materials and methods

4.2.1 Soil columns

Soil columns were taken from typical agricultural field consisting sandy-loam soil in Yanggu, Gangwon Province, South Korea (Soil C: 38.2°N, 128.13°E, Soil D: 38.2°N, 128.12°E). All soil columns are anthrosols also considered typical Korean cambisols (IUSS Working Group WRB 2007) due to regular artificial addition of soils on the fields to compensate for soil loss during monsoon season. Properties of soil columns are given by Table 4.1.

Table 4.1 Physical and chemical soil properties of soil columns

	Soil C -undisturbed	Soil C -disturbed	Soil D -undisturbed	Soil D -disturbed
Texture (%)[a]				
	Sand: 63.7	Sand: 63.7	Sand: 54.1	Sand: 54.1
	Silt: 27.1	Silt: 27.1	Silt: 35.6	Silt: 35.6
	Clay: 9.2	Clay: 9.2	Clay: 11.3	Clay: 11.3
Bulk density(g/cm^3)	1.39	1.28	1.42	1.26
Organic carbon (%)	4.41	4.41	2.34	2.34
pH	6.1	6.1	6.4	6.4

[a] According to soil texture classification system from USDA(United States Department of Agriculture).

4.2.2 Chemicals and reagents

Sulfadimethoxine was purchased from Sigma-Aldrich (Seelze, Germany). Isotope-labelled compound (Sulfadimethoxine-D_4) was obtained from Toronto Research Chemicals Inc.

(North York, Ontario, Canada). Brilliant blue FCF and KBr were purchased from Syntharo Fine Chemicals GmbH (Troisdorf, Germany) and Merck (Darmstadt, Germany). Methanol, acetonitrile and water for HPLC-MS-MS analysis were purchased from Th. Geyer GmbH (Renningen, Germany).

4.2.3 Soil column experiment

Solute and tracer experiment was conducted with disturbed and undisturbed soil columns. Fig. 4.1 shows the experimental setup. For preparation of the disturbed soil columns, soil taken in agricultural region (Yanggu, South Korea) sieved with 2mm mesh, and then packed into stainless steel cylinder with 30cm length and 15cm diameter. Undisturbed soil columns were taken from the same agricultural fields. 0.1M NaCl solution and deionized water was sequentially applied to soil column for 24hr in order to obtain hydraulic parameters of soil columns.

Leachate from the soil columns was collected every 5 minute in 30ml glass vial. Concentration of chloride ion in the aqueous sample was measured with conductivity meter (KLE 325, WTW GmbH, Weilheim, Germany).

At the end of test for chloride breakthrough curve, aqueous solutions with sulfadimethoxine (25mg/L), Brilliant blue FCF (1g/L) and KBr (20g/L as Br) were sprayed to disturbed and undisturbed soil column for 4hr. Precipitation rate of aqueous solution into soil columns was controlled by peristaltic pump with 5.6ml/min. HYDRUS-1D was chosen for the sake of simulating water flow and estimating hydraulic parameters in soil columns. HYDRUS-1D (Version 4.15, PC-Progress s.r.o.) couples water flux and solute transport in aqueous phase in accordance with Richardson equation and advection-dispersive equation.

To investigate the solute flow patterns, soil columns were horizontally cut at every 1.5cm depth intervals after column experiment. The cutting surfaces were photographed with a digital camera. The digital photos of soil were obtained with grey panel and calibration colour panel (Kotak Ltd., München, Germany) used to correct inhomogeneous illumination. The surfaces were sampled at both stained area and unstained area using a knife in order to determine concentration of sulfadimethoxine and tracers.

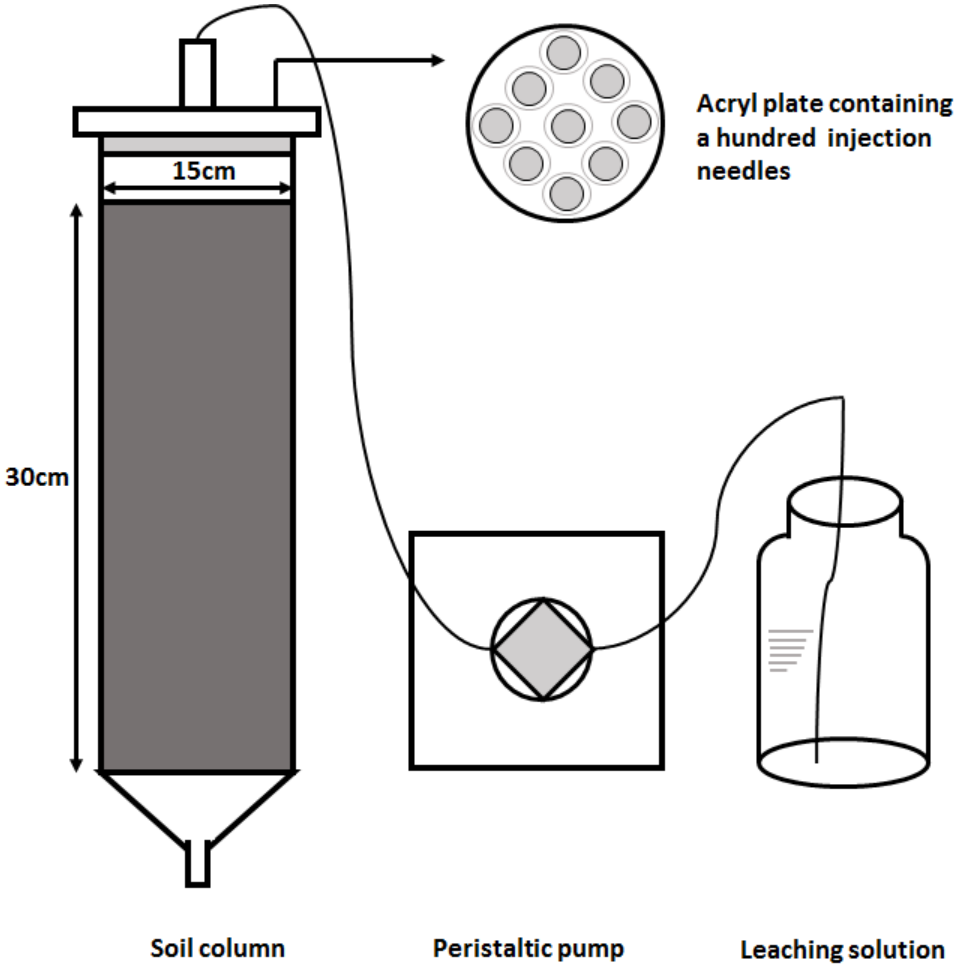


Fig. 4.1 Experimental setup for soil column studies

Weight of the sliced soils was determined before and after drying at 105℃ for water contents and dry bulk density. After drying, the slices were homogenized, and then measured concentration of sulfadimethoxine and tracers.

4.2.4 Batch sorption experiments

Soils were collected from agricultural region in Yanggu, Korea. The soils were transported to the laboratory, and were dried in 60℃. Properties of the soils was measured, such as particle distribution, carbon contents and pH. Particle distribution measurement was performed by laser diffraction analyser (Mastersizer S MAM5004, Malvern Instrument GmbH, Herrenberg, Germany), respectively. Soil properties are already given in Table 4.1.

Target chemical solutions were prepared using sulfadimethoxine dissolved in methanol. Sorption studies were performed in 30ml glass tubes operated as completely mixed batch system. Three replicate tubes were prepared for each treatment by adding 2g of dry soil and 10ml of working solution containing 0.01M KBr_2 to pre-weighed tubes. Losses caused by sorption were quantified with control tubes that contained no soil materials. The soil-solute mixtures were homogenized with a shaker at room temperature for 24 hr. A preliminary adsorption experiment was performed in order to determine contact time required for adsorption equilibrium. Within 24 hr, equilibrium of all tracers was reached regardless of soil type (not shown in this paper). At the end of the contact time, the tubes were centrifuged for 20min at 1500rpm and then the aliquots were filtered with 0.22μm PES membrane (Millipore, Billerica, MA). The antibiotics remaining in the aliquot was measured by HPLC-MS-MS.

The experimental data of the equilibrium adsorption isotherm for the sulfonamides were represented by Freundlich isotherm model considering multilayer adsorption over heterogeneous surface. Freundlich isotherm is given as:

$$q_e = K_f C_e^{1/n}$$

where q_e is amount of adsorbate in the adsorbent at equilibrium (mg/g), and C_e

represents equilibrium concentration (mg/L). K_f is Freundlich isotherm constant (mg/g), and 1/n is adsorption intensity related to adsorption capacity.

4.2.5 Analysis of antibiotics and bromide

Sulfadimethoxine in soil samples were analysed using HPLC-MS-MS (Quattro micro TM API, Waters, Milford, MA). Sulfadimethoxine-D_4 was used as internal standard. Pretreatment of soil samples is described as follow. 2g Soil was placed into 5ml methanol, 5ml acetate buffer (pH 4.0) and 0.2ml 0.005M EDTA. Each sample was mixed for 3 min and then sonicated for 30 min before centrifuged at 1500rpm for 10 min. The above extraction was conducted 2 times to enhance extraction efficiency of the sulfonamides. The extract was also dissolved in 200ml deionized water to minimize the solvent effect on the further extraction procedure. Through solid phase extraction (SPE) using OASIS HLB cartridge (Waters, Milford, MA), the target antibiotics was more concentrated in 1ml extraction (acetonitrile: water, 3:7).

Brilliant blue concentration in soils was estimated by extraction method with water-acetone solution (Diallo 2011). For extraction of brilliant blue, the 1g soil dried in oven (105℃) was shaken with 50 ml water- acetone solution (4:1) for 10 minutes. The mixture was centrifuged at 1500 rpm for 20 minutes, and then the aliquot was collected. The above extraction procedure was repeated 3 times. Brilliant blue concentrations in aliquots were determined with spectrophotometer at 628nm (CARY 100 Conc, Varian Inc., CA, USA).

Bromide was extracted by shaking 2g dried soil with 50ml water for 30 minutes. The suspensions were centrifuged at 1500 rpm for 20min, and then the separated aliquots were collected. Bromide concentration was measured with ion-selective electrode (Metrohm, Zofingen, Switzerland) for bromide in combination with reference electrode.

4.2.6 Image processing

The whole pixel number of original images was reduced by smoothing method suggested by Kasteel et al. (2013). Pixel size of the modified images was 0.58×0.58 mm^2, and geometrical distortion was not observed. Background subtraction using value V of grey panel was a proper method to minimize the effect of inhomogeneous illumination. Thus, RGB values were taken on four corners of grey panel, and then were transformed into HSV (hue, saturation, value) colour system (Kasteel et al., 2013). The analysis for inhomogeneous illumination showed that V values rarely varied in images, and were almost constant among all images. Consequently, correction was not conducted for inhomogeneous illumination.

In order to estimate the dye coverage of horizontal cutting images, we followed conditional dilation method (Serra, 1998). In the method, upper and lower thresholds are used to homogenize stained area by integrating single dye pixels to adjacent larger dye patterns. The upper and lower classes belong to each stained area and background. Pixels belonging to uncertainty range result from the two classes relying on adjacent pixels. This method is repeated iteratively until no uncertain pixels is found. Isolated single pixels, which are not neighboured with larger dye patterns are removed. Eventually, the conditional dilation method leads to enhanced spatial coherence and lower noise interference for images.

4.3 Results and Discussions

4.3.1 Adsorption and breakthrough curve of sulfadimethoxine and tracers

In the batch sorption experiment, equilibrium of all tracers was reached within 24 hr regardless of soil type. Detectable degradation was not observed in supernatant during adsorption experiment. Therefore, the reduction of the testing materials was considered to be

owing to adsorption onto soil. Adsorption isotherms of sulfadimethoxine and the tracers were non-linear and well fitted with Freundlich isotherm, as given in Table 4.2.

Table 4.2 Adsorption parameter of sulfadimethoxine, brilliant blue FCF and bromide based on Freundlich isotherm (standard error)

Compounds	Soil	K_d	K_f	1/n	R
Sulfadimethoxine					
	Soil C	1.78 (0.03)	1.89 (0.02)	0.87 (0.02)	0.99
	Soil D	1.62 (0.03)	1.74 (0.02)	0.84 (0.03)	0.99
Brilliant blue FCF					
	Soil C	2.97 (0.03)	3.59 (0.40)	0.96 (0.02)	0.99
	Soil D	2.51 (0.02)	2.42 (0.22)	1.00 (0.02)	0.99
Bromide					
	Soil C	0.0042 (0.0002)	0.0068 (0.001)	0.94 (0.15)	0.98
	Soil D	0.0044 (0.0002)	0.018 (0.02)	0.84 (0.14)	0.96

Sulfadimethoxine was adsorbed weaker than Brilliant blue FCF to all soils. Bromide was hardly sorbed to all test soils, compared to sulfadimethoxine and brilliant blue FCF. Adsorption of the organic compounds was dependent on the soil organic matter. For acidic organic compounds, several previous studies have proved that soil organic carbon is most important soil property to depict sorption behaviour (Tolls, 2001; Villaverde et al., 2008). For example, the strength of sorption for sulfamethazine correlated with organic matter and pH (Fan et al., 2011), and k_d of acid pesticides (e.g. 2.4-D and dicamba) increased as increasing soil organic carbon (Villaverde et al., 2008). Soil texture and pH of soil did not affect the

sorption reaction. Mineral blockage by soil organic matter may results in reduction of binding capacity between mineral component (e.g. clay, Fe-oxides) and adsorbates (Villaverde et al., 2008). Due to very low sorbility, sorption of bromide is rarely affected by organic matter as well as clay content.

4.3.2 Estimation of water flow

For each soil column, the hydraulic parameters was estimated through inverse modelling based on Cl^- tracer experiment and dual porosity model in Hydrus 1-D. Dual porosity model assumes that water flow is restricted to mobile region (e.g. macropore and inter-aggregate pore), and water in matrix is stagnant. Conservative tracers are frequently used to track water flow in soil system as well as to determine hydraulic parameters (Leaney et al., 1993; Fesch et al., 1998).

Table 4.3 Hydraulic parameter of soil columns

Soil column	θr (m^3/ m^3)	θs (m^3/ m^3)	K_s (m/hr)	α (m^{-1})	n (-)
Soil C (undisturbed)	0.048	0.401	0.0278	3.66	1.54
Soil C (disturbed)	0.044	0.391	0.0236	3.51	1.52
Soil D (undisturbed)	0.068	0.422	0.0141	4.05	1.58
Soil D (disturbed)	0.062	0.415	0.0114	3.87	1.57

Cl^- concentration of leachate from disturbed soil column was recorded lower value then from natural soil column, until the concentration reached at maximum value. In the present study, Cl^- coming from soil matter did not hardly affect chloride breakthrough curve, regardless of soil origin. In the phase of deionized water application, Cl^- in disturbed soil column was

leached slower than in disturbed soil column due to lower pore water velocity and dispersion.

Table 4.4 Goodness-of-fit measures for simulations and observed data

Soil column	Data set	RMSE[a]	MAE[b]	R^2
Soil C (undisturbed)	Cl in leachate	0.144	0.021	0.999
Soil C (disturbed)	Cl in leachate	0.126	0.016	0.999
Soil D (undisturbed)	Cl in leachate	0.437	0.190	0.993
Soil D (disturbed)	Cl in leachate	0.300	0.090	0.996

[a] Root mean square error, $\text{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(S_i - O_i)^2}$, [b] Mean absolute error, $\text{MAE} = \frac{1}{n}\sum_{i=1}^{n}|S_i - O_i|$

Earthworms and roots play important roles in generating water flow channels. Most of macropores (e.g. earthworm tunnel and root channel) were destroyed during homogenizing and packing procedures, and the contribution of water flow in macropore was minimized. Consequently, lower water permeability was observed in disturbed soil column, compared to natural soil column. In particular, hydraulic conductivity values were affected by soil disturbance, ranging from 1.17 to 1.31 times higher than that in undisturbed columns, as shown in Table 4.3. The disturbance was hardly influenced to α and n values in the parameter estimation. Table 4.4 gives goodness-of-fit measures between the simulated and observed values for chloride concentrations in leachates. The inverse solution with the chloride leaching provided the proper correlation for the hydraulic parameters.

4.3.3 Depth profile of sulfadimethoxine and tracers

Depth profiles of sulfadimethoxine and tracers were given in Fig. 4.2, 4.3 and 4.4. As a consequence, the profiles show that distribution of the antibiotics and tracers is dependent on water flow as well as adsorption of the applied compound. The depth profile illustrates that sulfadimethoxine and BB was leached relatively slow into the soil column by water.

For each horizontal cutting section, we took 1-3 samples (2-3g) from both stained and unstained area to analyse the residual concentrations (Table 4.5, Table 4.6). We also analysed the concentrations of the applied compounds, as well as the whole bulk concentrations in each cutting slice. The residue of sulfadimethoxine in the all soil columns was concentrated in stained area in the each horizontal cutting section. For both undisturbed and disturbed soil D, no antibiotics was detected below each 25cm and 20cm depth, although existence of brilliant blue FCF and dye covered area was observed in soil slices. Mixing procedure between stained and unstained area can lead to reduce concentration of the antibiotics residue under detection limit. Due to adsorption of sulfadimethoxine and brilliant blue FCF, lateral transport of the solutes was limited in all soil columns. Except for 0-4.5 cm depth of all soil columns where the soil was almost fully stained, the concentration in stained area was 7-30 times higher than in unstained area. In contrast, bromide distribution was more homogeneous than sulfadimethoxine in each soil section. For samples chosen from unstained area, the local concentrations were frequently as high as in dye-stained area. This points out that the non-adsorbable tracer spread more in lateral direction without any reactions between the tracer and soil matter. For applied compounds, the lowest local concentration was assigned to samples taken from unstained area in all depth.

In the study, different vertical mobility of sulfadimethoxine and two tracers can be also inferred from depth profiles of their concentration. The depth profile offers that sulfadimethoxine and BB are less mobile than bromide in all soil columns. Nevertheless, vertical distribution of the antibiotics and dye did not coincide with their mobility predicted from the adsorption isotherm and hydraulic parameters. For all columns from 9 cm to bottom, their residual concentration is relatively higher than simulated value. This implies that transport of sulfadimethoxine and BB was non-equilibrium. The comparison of depth profile between disturbed and undisturbed column shows that soil disturbance reduced longitudinal dispersion

of sulfadimethoxine and two tracers.

Table 4.5 Residual concentrations of sulfadimethoxine, BB and Br for soil C columns

Column	Depth	Stained/unstained	Sulfadimethoxine (mg/kg)	BB (mg/kg)	Br (mg/kg)
Undisturbed	0 cm	Stained	15.5	451.1	1.14
	0 cm	Stained	16.1	425.7	1.27
	6 cm	Stained	6.4	240.3	1.01
	6 cm	Stained	7.2	274.9	1.05
	6 cm	Stained	5.8	235.8	1.07
	15 cm	Stained	1.1	76.7	0.97
	15 cm	Stained	0.9	64.5	1.03
	15 cm	Unstained	ND[a]	ND	0.44
	15 cm	Unstained	0.2	ND	0.23
	27 cm	Stained	0.1	3.77	0.71
	27 cm	Unstained	ND	ND	0.38
	27 cm	Unstained	ND	ND	0.51
Disturbed	0 cm	Stained	19.2	558.1	1.99
	0 cm	Stained	16.9	514.6	2.01
	6 cm	Stained	8.6	301.5	1.61
	6 cm	Stained	8.3	274.6	1.51
	6 cm	Stained	7.7	262.2	1.48
	15 cm	Stained	2.0	97.8	1.09
	15 cm	Stained	2.2	104.2	1.24
	15 cm	Unstained	0.8	ND	0.81
	15 cm	Unstained	ND	ND	0.48
	27 cm	Stained	0.1	1.7	0.49
	27 cm	Unstained	ND	ND	0.24
	27 cm	Unstained	ND	ND	0.15

[a] ND: not detected.

Table 4.6 Residual concentrations of sulfadimethoxine, BB and Br for soil D columns

Column	Depth	Stained/unstained	Sulfadimethoxine (mg/kg)	BB (mg/kg)	Br (mg/kg)
Undisturbed	0 cm	Stained	16.5	546.8	1.61
	0 cm	Stained	19.3	598.2	1.64
	6 cm	Stained	7.8	295.2	1.55
	6 cm	Stained	8.4	368.7	1.58
	6 cm	Stained	8.6	384.1	1.62
	15 cm	Stained	2.0	170.1	1.54
	15 cm	Stained	1.6	112.6	1.34
	15 cm	Unstained	0.3	ND[a]	0.71
	15 cm	Unstained	0.2	ND	0.64
	27 cm	Stained	0.2	9.9	1.04
	27 cm	Unstained	ND	ND	0.51
	27 cm	Unstained	ND	ND	0.48
Disturbed	0 cm	Stained	19.5	857.0	2.68
	0 cm	Stained	17.2	791.2	2.59
	6 cm	Stained	9.1	594.7	2.24
	6 cm	Stained	7.8	488.6	2.14
	6 cm	Stained	8.7	574.1	2.16
	15 cm	Stained	2.6	6.7	1.61
	15 cm	Stained	1.8	5.3	1.61
	15 cm	Unstained	0.4	ND	1.14
	15 cm	Unstained	0.1	ND	0.71
	27 cm	Stained	0.1	1.2	0.62
	27 cm	Unstained	ND	ND	0.31
	27 cm	Unstained	ND	ND	0.33

[a] ND: not detected.

Mass recoveries are given as partitioning ratio between soils and leachate after applying the sulfadimethoxine and tracers. The overall mass recovery, which is the sum of residual ratio

in soils and in leachate, ranged between 95% and 100% for the all compounds. In particular, overall mass recovery was high for sulfadimethoxine and the dye tracer, since short precipitation time (4hr) restrained biodegradation for the organic compounds on soil columns. The conservative tracer, bromide was also rarely lost during the solute transport, regardless of soil properties and structure.

Table 4.7 Mass recovery of sulfadimethoxine, brilliant blue FCF and bromide

Soil	Structure	Sulfadimethoxine (%)		Brilliant blue FCF (%)		Bromide (%)	
		Soil	Leachate	Soil	Leachate	Soil	Leachate
Soil C	Undisturbed	62.3	35.8	66.7	30.6	24.9	74.8
	Disturbed	83.9	15.5	73.2	24.1	30.6	68.9
Soil D	Undisturbed	87.4	12.1	83.4	15.1	36.7	63.1
	Disturbed	93.2	6.1	90.0	9.2	40.6	58.8

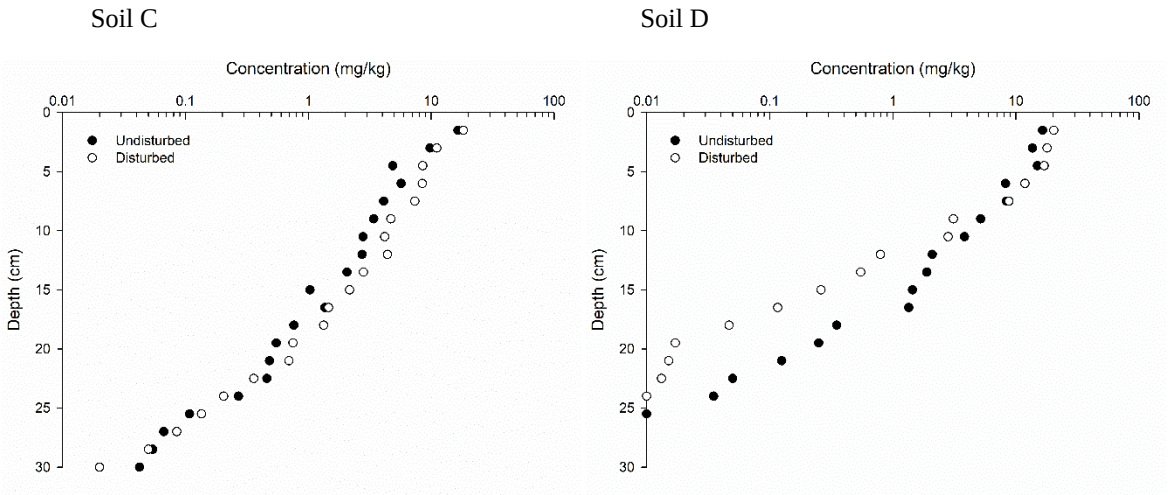


Fig. 4.2 Sulfadimethoxine distribution in undisturbed and disturbed soil column profile of Soil C and D

Soil C

Soil D

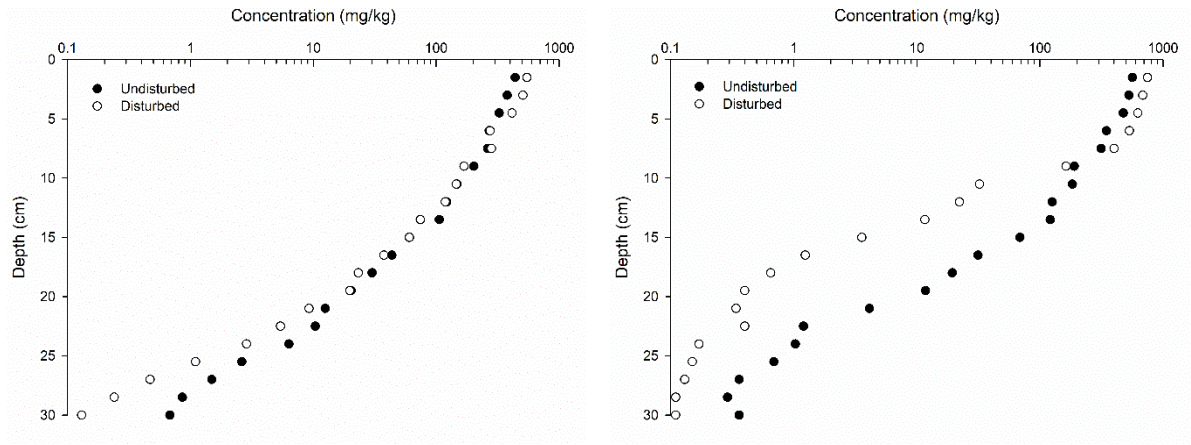


Fig. 4.3 Brilliant blue FCF distribution in undisturbed and disturbed soil column profile of Soil C and D

Soil C

Soil D

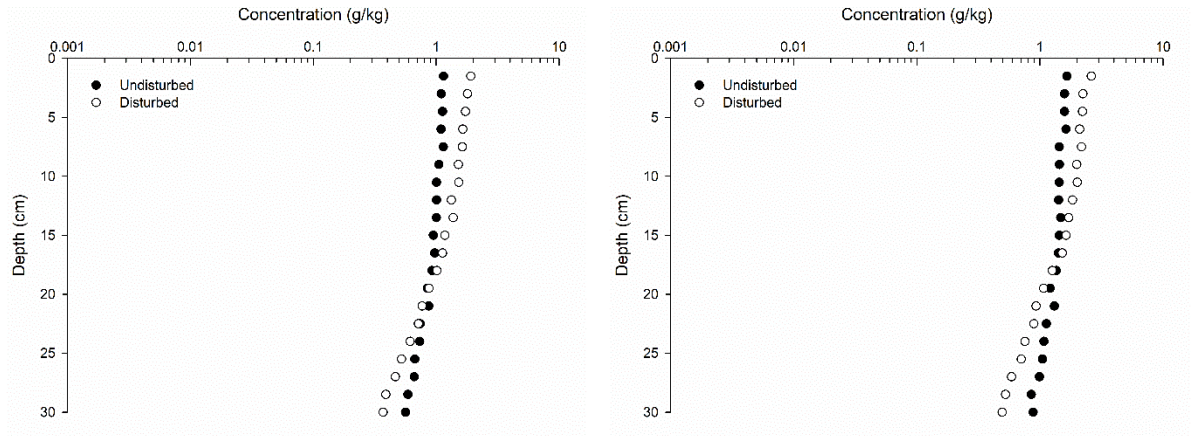


Fig. 4.4 Bromide distribution in undisturbed and disturbed soil column profile of Soil C, D and E

4.3.4 Dye staining

Brilliant blue FCF visualized heterogeneity of the solute transport by staining parts of the bulk soil where it contacted with the dye solution. Fig. 4.5 and 4.6 shows these staining patterns in horizontal cross-sections at depths for the testing soils.

For all testing soils, dye coverage was almost 100% to upper 6cm. From full dye covered depth downward, ratio of dye coverage decreased for all soils, ranging from 7.3% to 91%. Near bottom of soil column, the value exceptionally increased owing to boundary of soil-water and air interface. For undisturbed soil column C, full dye coverage section was observed from top to 6cm depth as similar to disturbed soil column. From 7.5cm to 24cm depth, ratio of dye coverage for undisturbed soil column C was smaller than for disturbed soil column C. Below 24cm depth, dye coverage for disturbed soil C column area dramatically decreased in range from 65.3% to 12.09%, where the value varied within 8% for the undisturbed soil column. The dye pattern might correspond to distribution flow was dominant at upper and mid depth region, instead of preferential flow. The overall dye pattern was obviously different between undisturbed and disturbed soil D column. The ratio of dye coverage for the undisturbed soil column D was higher than for the disturbed soil column D except for first 6cm depth, where the monolith for both columns was almost fully stained.

Flühler et al. (1996) described different flow regimes based on phenomenological transport feature, which is dominated by one or more transport mechanisms as follows: (ⅰ) distribution flow in the attractor zone where flow convergence is initiated, (ⅱ) preferential flow in the transmission zone where flow is selectively faster than convective transport, (ⅲ) dispersive flow in the dispersion zone where lateral mass exchange is not negligible, and can eventually lead to divergence of the transport. The first 4.5cm of all soil columns can be regarded as attractor zone, where partitioning of BB to preferential flow channels is initiated.

For undisturbed soil columns, this corresponds to higher porosities and loosened soil structure in the top layers to weather events (e.g. precipitation, wind). Under the attractor zone, transmission zone was located, where BB was transported in isolated flow path. Density of preferential flow channel can affect lateral transport of solute in the undisturbed column. Vanderborght et al. (2002) found density of macropore affects lateral transport of solute in soil, with investigating transport of fluorescent tracers and dye coverage. They reported that dense network of macropore can induce lateral spreading of solute. In contrast, lateral dispersion was limited in soil where fewer macropore was developed. The observed dye patterns in our study were related to the density of macropore channels. A study on unsaturated flow showed that lateral dispersion is more intense in coarse than in fine porous media for steady-state flow (Koch and Flühler, 1994).

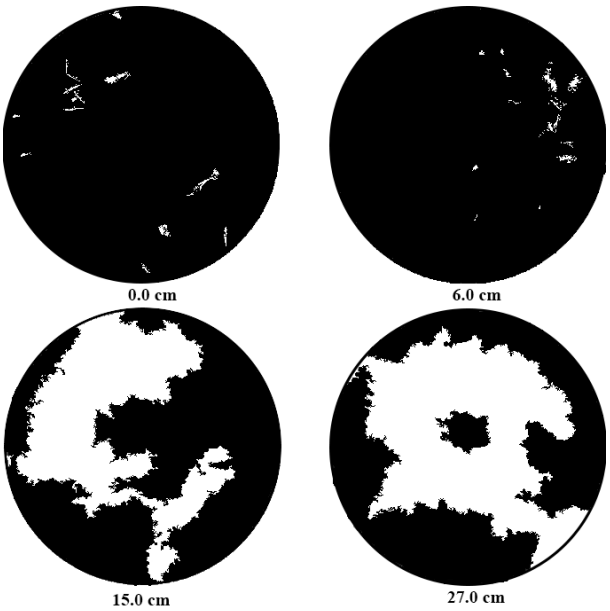
Preferential flow was limited in disturbed soil column, as macropore channels were destroyed by sieving and soil mixing. Partly, the presence of the cylinder wall acted as preferential flow path in the disturbed soil, and no preferential flow path was observed in inner area of both disturbed soil C and D. For the disturbed soil, dye coverage in the transmission zone indicated the disturbance of lateral dispersion by the wall.

The dye patterns of all experiment column showed that non-equilibrium adsorption was dominant for BB and sulfadimethoxine. Partial fast flow leaded to non-equilibrium process, and eventually reduced amount of the adsorbed solutes onto soil material. Sulfadimethoxine distribution did not exactly corresponded with BB and bromide distribution. As shown in our batch sorption test, BB has higher sorbility than the antibiotics. In adsorption kinetic test, we found that BB and sulfadimethoxine reached at equilibrium point within each 3hr and 9hr (data not shown). Nevertheless, lateral spreading of the antibiotics was visualized with applying BB for some extent, due to acceptable similarity of sorbility between BB and the antibiotics. In

contrast, lateral transport of bromide did not present lateral transport of the antibiotics, even though the ionic tracer more properly depicted water movement.

Dye coverage did not coincided with amount of residual BB in each cross-section. Obviously, the dye intensity was dependent on values of RGB colour channel. Nevertheless, concentration of BB cannot be quantified with image analysis in the present study, since no date were available in order to correlate between the value of colour channel and BB concentration.

Soil C - undisturbed



Soil C - disturbed

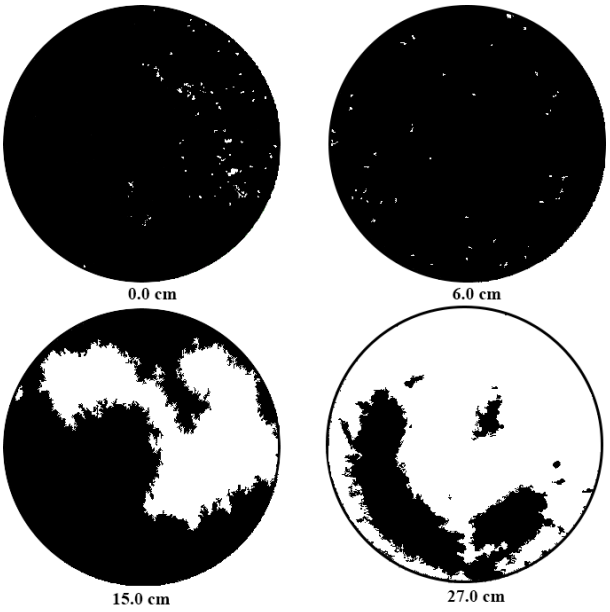
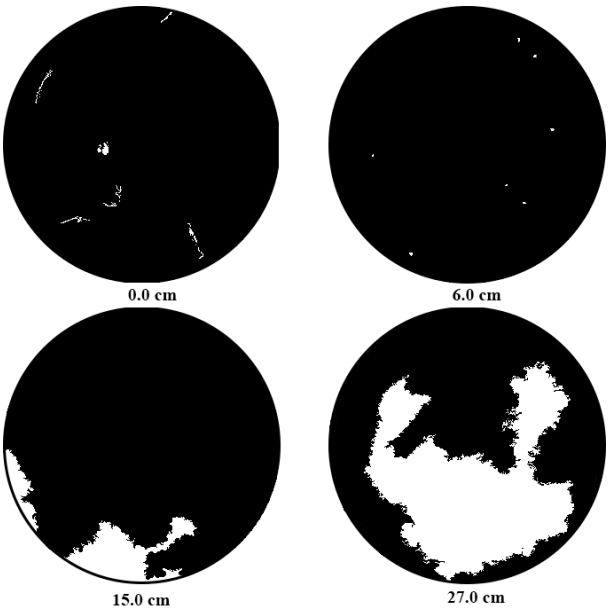


Fig. 4.5 Dye patterns from horizontal cross-section for soil columns by Brilliant blue FCF for Soil C columns

Soil D - undisturbed



Soil D - disturbed

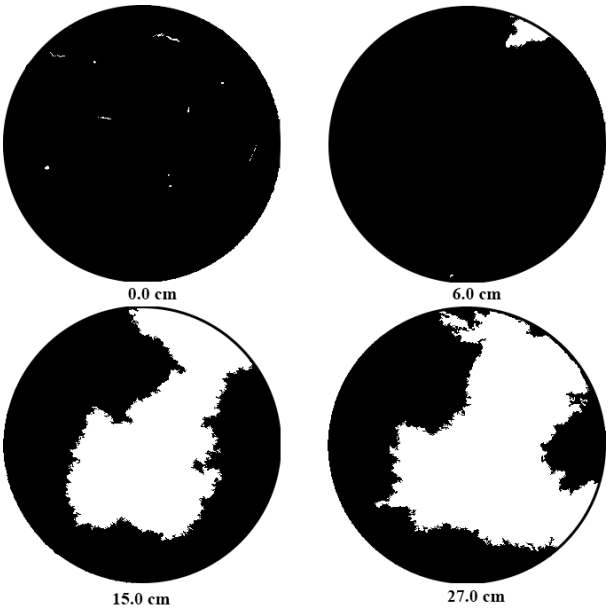


Fig. 4.6 Dye patterns from horizontal cross-section for soil columns by Brilliant blue FCF for Soil D columns

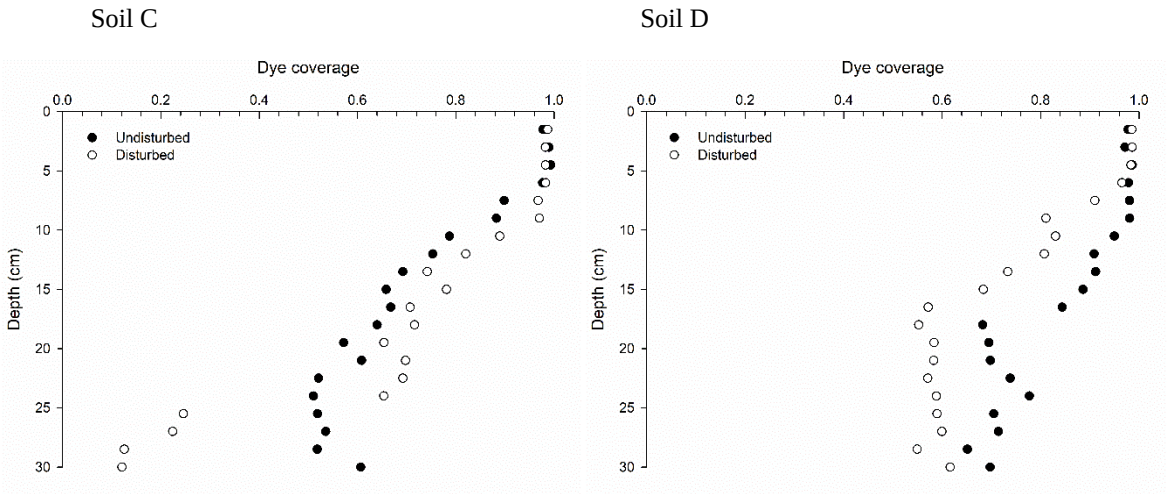


Fig. 4.7 Dye coverage in soil column profile of soil columns by Brilliant blue FCF

4.4 Conclusions

Visualization of transport pathway with BB is useful to extend understandings of sulfadimethoxine transport phenomena in soil system. The dye pattern in horizontal cross-sections revealed that macropore and preferential transport pathways can be used as major transport pathway of the organic compound. Combination of the image processing and selective sampling for chemical analysis can also define spreading regions of adsorbable and non-coloured solutes. Different distribution between the adsorbed tracer (BB) and non-adsorbed tracer (bromide) showed that water movement does not coincide with transport behaviour of the adsorbable compounds. Both lateral and vertical mass transfer of bromide were higher compared to BB and the sulfonamide, which needs more time to reach accessible flow regions than bromide. In contrast, sulfadimethoxine distribution can be interpreted with BB distribution, since transport behaviour of BB was retarded by adsorption in soil-water interface as of the antibiotics. Therefore, BB can be alternatively used as a surrogate *in situ* for interpretation of transport behaviour of sorbable organic pollutants, which have toxicological concerns. Our findings showed that other dye tracers may also be applicable to identify transport pathways of various organic contaminants, of which physico-chemical properties are similar to those of the dye tracers.

Disturbance of soil destroyed preferential flow path. This eventually leaded to stagnant of the solute and water movement. Structure-dependent flow in undisturbed soils is the major process determining the transport process of the low mobile solutes. Since a small fraction of the soil was involved in preferential flow, the water movement through the small region are faster than when the entire volume of the soil was involved in the water flow. The sorption process was kinetically limited due to short contact time with soil materials. The rapid water flow in macropore results in non-equilibrium adsorption, and consequently increase mobility of organic solutes. Therefore, soil structure should be considered to explain fate of organic

solutes as well as their physico-chemical properties.

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Declaration / Erklärung

Erklärung zur Promotionsarbeit:

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Hiermit erkläre ich, dass ich die vorliegende Promotionsarbeit selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

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